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transferred from the trap to the coil in the usual way and its pressure was measured.

The time of analysis was slightly longer, but the use of liquid air instead of liquid oxygen as the coolant caused no difficulty.

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V. Ramakrishna*

1 Methods of Analysis Committee Report, *J. Iron Steel Inst. London*, 183 (1956) 287.
2 R. M. Cook and G. E. Speight, *Analyst*, 81 (1956) 144.
3 *International Critical Tables*, vol. III (1928) 203.
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ERRATA

Anal. Chim. Acta, 20 (1959) 406, under *Vacuum weighing correction*, the equations should read:

$$W_{s_1} - W_{s_1} \times d_a/d_1 = W_{s_2} - W_{s_2} \times d_a/d_2$$

$$\therefore W_{s_1}/W_{s_2} = \frac{d_2 - d_a}{d_1 - d_a} \times \frac{d_1}{d_2}$$

The error incurred by ignoring vacuum correction will be:

$$\frac{1 - W_{s_1}/W_{s_2}}{1} = \frac{d_a(d_1 - d_2)}{d_2(d_1 - d_a)} \approx \frac{d_a(d_1 - d_2)}{d_1 d_2} \approx d_a(d_1 - d_2)$$

Following paragraph, line 4, should read: . . . . . the error incurred is 2.42 (instead of 2.44) in 10^6, ...
lines 7 and 8 should read: . . . . . the error is still only 10.9 in 10^6, or 0.00109%.

THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VIII. THE EFFECT OF SUBSTITUENTS IN THE NAPHTHALENE NUCLEUS ON THE FLUORIMETRIC DETECTION OF TIN

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INTRODUCTION

In previous papers of this series[1–8], naphthalene derivatives have been used for the detection and determination of inorganic ions. In particular, the qualitative and quantitative applications of the substituted nitronaphthalenes as fluorimetric reagents for stannous tin have been reported[1–7]. This paper summarizes the effect of various electropositive and electronegative substituents in the nitronaphthalene nucleus upon the intensity of fluorescence in this test. The compounds investigated in this series of reactions include dinitronaphthalenes, dinitronaphthylamines, halogen substituted mononitronaphthylamines, mononitroso- and dinitronaphthols and

TABLE I

Reagents used for spraying spots of metallic salts

Reagent No.	*Reagent*
	0.1% solution in a mixture of equal volumes of 96% ethyl alcohol and 10 N HCl
1	1-nitronaphthalene
2	2-nitronaphthalene
3[a]	1,5-dinitronaphthalene
4	1,8-dinitronaphthalene
5	4-nitro-2-iodo-1-naphthylamine
6	2-nitroso-1-naphthol
7	4-nitroso-1-naphthol
8	1-nitroso-2-naphthol
9	2,4-dinitro-1-naphthol
10[b]	1,7-dinitro-2-naphthol
	0.1% solution in a mixture of 3 volumes of 96% ethyl alcohol and 1 volume 10 N HCl
11	2-nitro-4-chloro-1-naphthylamine
12	2,4-dinitro-1-naphthylamine
	0.1% aqueous solution
13	1-nitroso-2-naphthol-3,6-disulphonic acid
14	2,4-dinitro-1-naphthol-7-sulphonic acid

[a] Since 1,5-dinitronaphthalene was soluble in alcohol to less than 0.1%, a saturated alcoholic solution was employed. A 0.1% solution of the reagent in benzene was also found to be satisfactory.

[b] B.D.H. Laboratory reagent.

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their sulphonic acid derivatives. The results confirm the previous conclusions that the intensity of the fluorescence depends markedly upon two factors (a) the nature of the substituent present, *i.e.* electropositive or electronegative and (b) the position of the substituent in the naphthalene ring.

EXPERIMENTAL

Reagents

All reagents used were commercially available except 2-iodo-4-nitro-1-naphthylamine and 4-chloro-2-nitro-1-naphthylamine.

2-Iodo-4-nitro-1-naphthylamine, was prepared by heating 4-nitro-2-acetoxymercuri-1-naphthylamine with iodine in aqueous potassium iodide according to the method of HODGSON AND ELLIOTT[9].

4-Chloro-2-nitro-1-naphthylamine, synthesized by the chlorination of 2-nitro-4-acetoxymercuri-1-naphthylamine dissolved in acetic acid[10].

Spot-test procedure

Experiments were performed using the same spot-test procedure as outlined in a previous communication[5].

The reagents employed are listed in Table I.

RESULTS

The results of the tests are summarized in Table II. The effect of strong hydrochloric acid upon the intensity of the fluorescence is reported in Table III.

TABLE II

Fluorescence obtained on spraying spots of ions with various reagents after treatment with 15 *N* NH_4OH

Ion	*Reagent number*													
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
Sn^{+2}	SF	F	F	F	WF	VWF	WF	SF	WF	WF	SF	F	SF	WF
	(B)	(P)	(P.B)	(P.B)	(G.Y)	(P.B)	(P.B)	(B)	(P.R)	(Br.O.G)	(Y.G)	(P.R)	(G.B)	(P.R)
Sb^{+3}													WF	
[a]Ce^{+4}														WF
Mo^{+6}								WF						
W^{+6}								WF					WF	
$VO^{+?}$													WF	
VO_4^{-3}													WF	
ZrO^{+2}						WF								
Zr^{+4}						WF								
Ti^{+3}								WF					WF	

[a] A solution of ceric ammonium nitrate (Analar) in 3 *N* H_2SO_4 was used.

Fluorescence key

SF = Strong fluorescence
F = fluorescence
WF = Weak fluorescence
VWF = Very weak fluorescence

Colour key

B = Blue
G = Green
R = Red
Br = Brown
P = Purple
Y = Yellow
O = Olive.

Other ions tested included:

Be^{+2}, Ca^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2}, Sn^{+4}, As^{+3}, As^{+5}, Bi^{+3}, Fe^{+2}, Fe^{+3}, Al^{+3}, Cr^{+3}, Cr^{+6}, Cu^{+2}, Co^{+2}, Ni^{+2}, Hg^{+}, Hg^{+2}, Pb^{+2}, Ag^{+}, Ce^{+3}, Cd^{+2}, Mn^{+2}, Ti^{+4}, Th^{+4}, La^{+3}, Pd^{+2}, Pt^{+2}, Pt^{+4}, Au^{+3}, Ru^{+3}, In^{+3}, Tl^{+}, Tl^{+3}, UO_2^{+2}, VO_3^{-}, Rb^{+}, Cs^{+}, Li^{+}, K^{+}, Na^{+}, Zn^{+2}.

These ions gave either no fluorescence or coloured spots with only a faint trace of fluorescence.

Ions which gave no fluorescence with the reagents were:

Fe^{+2}, Cr^{+3}, Mn^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2}, K^{+}, Rb^{+}, Ce^{+3}, Au^{+3}, Pd^{+2}, Tl^{+}, Tl^{+3}, VO_3^{-}, Ag^{+}.

TABLE III

Effect of HCl upon the intensity of fluorescence of spots, (0.01 ml), containing 10^{-4} g stannous tin

Reagent number in Table I	*0.1% Solution of reagent in*			
	Alcohol		*50/50 v/v Alcohol/10 N HCl*	
	B	*A*	*B*	*A*
1	VWF	F	WF	SF
2	VWF	F	WF	F
3	WF	WF	F	F
4	WF	WF	F	F
5	VWF	VWF	WF	WF
6	VWF	VWF	VWF	VWF
7	WF	WF	WF	WF
8	WF	F	WF	SF
9	VWF	WF	VWF	WF
10	VWF	WF	VWF	WF
11	VWF	F	WF	SF
12	VWF	VWF	WF	F
13			F	SF
14			VWF	WF

B = Before spraying with 15 N NH_4OH
A = After spraying with 15 N NH_4OH

The above results indicate that as previously reported for other reagents[6,7], the presence of concentrated HCl is advantageous for the fluorescent tin test.

Sensitivity tests

Sensitivity tests for stannous tin were carried out in the presence of hypophosphorous acid as previously described[1]. All the reagents tested exhibited a distinct fluorescence with stannous tin, with the exception of reagent number 6 which gave a very weakly fluorescent purple coloured spot. The fluorescence shown by the reagents was essentially blue in colour, but with some compounds yellow-green, green-blue and purplish shades were also given. Reagent numbers 1, 8, 11 and 13 gave the most intense fluorescence, followed by reagent numbers 2, 3, 4 and 12, while reagent numbers 5, 7, 9, 10 and 14 gave only weakly fluorescent spots with stannous tin. All reagents were capable of detecting 10^{-4} g stannous tin and 10^{-5} g was detected with reagent numbers 1, 3, 5 and 13. Blank tests with all reagents on spots of 2% hypophosphorous acid showed no fluorescence under the conditions of the test.

DISCUSSION

The mechanism for the stannous chloride reduction of nitro groups in naphthalene compounds has already been discussed by HODGSON[11] in terms of a conventional nucleophilic reaction. The ease of monoreduction of polynitro-compounds was shown to be dependent on the electrophilic (positive) character of the nitro group which was preferentially attacked. This theory has been confirmed by OGATA AND SUGIYAMA[12] who studied the reduction velocities of para-substituted nitrobenzenes with stannous tin. These authors showed that the larger the electron-pulling force of the substituent in the para position, the faster was the rate of reduction of the nitro group.

From the results reported in this paper for nitronaphthalene derivatives, two of the most important factors associated with the reduction appear to be:

(a) the position of the nitro group in the naphthalene nucleus, *i.e.*, whether it is α- or β- or whether it is sterically hindered and (b) the electropositive or electronegative character of *other* substituent groups present in the compound.

To summarize the relative effect of some substituents in nitronaphthalene upon the sensitivity of the stannous tin test, the reagents used in this series of reactions have been classified into the following groups in Table IV. It will be observed that each group contains different type substituents.

TABLE IV

Summary of stannous tin reduction products of reagents

Group	*Reagent No. in Table I*	*Reagent*	*Reduction product with* Sn^{+2}	*Reference to reduction*	*Fluorescence with* Sn^{+2}
A	1	1-Nitronaphthalene	1-Aminonaphthalene	13	SF
	2	2-Nitronaphthalene	2-Aminonaphthalene	13	F
B	3	1,5-Dinitronaphthalene	1,5-Diaminonaphthalene No intermediate mono-reduction product	11, 14	F
	4	1,8-Dinitronaphthalene	1,8-Diaminonaphthalene No intermediate mono-reduction product	11, 14	F
C	6	2-Nitroso-1-naphthol	2-Amino-1-naphthol	15	VWF
	7	4-Nitroso-1-naphthol	4-Amino-1-naphthol	16	WF
	8	1-Nitroso-2-naphthol	1-Amino-2-naphthol	17	SF
	13	1-Nitroso-2-naphthol-3,6-disulphonic acid	1-Amino-2-naphthol-3,6-disulphonic acid	17	SF
D	12	2,4-Dinitro-1-naphthylamine	2-Nitro-1,4-naphthalenediamine	—	F
	9	2,4-Dinitro-1-naphthol	2-Nitro-4-amino-1-naphthol	18	WF
	10	1,7-Dinitro-2-naphthol	7-Nitro-1-amino-2-naphthol	—	WF
	14	2,4-Dinitro-1-naphthol-7-sulphonic acid	2-Nitro-4-amino-1-naphthol-7-sulphonic acid	18	WF
E	5	2-Iodo-4-nitro-1-naphthylamine	2-Iodo-1,4-naphthalenediamine	10, 19	WF
	11	4-Chloro-2-nitro-1-naphthylamine	4-Chloro-1,2-naphthalenediamine	10, 19	SF

It will be seen from the above table that the stannous tin reduction products of 2,4-dinitro-1-naphthylamine and 1,7-dinitro-2-naphthol have not been reported in the literature. On the basis of HODGSON's work[11,14,22] with the monoreduction of α, β-dinitronaphthalenes, particularly 1,3-dinitronaphthalene[22], the main product expected for the reduction of 2,4-dinitro-1-naphthylamine would be 2-nitro-1,4-naphthalenediamine together with a very small amount of 4-nitro-1,2-naphthalenediamine. This conclusion is confirmed by the reduction of 2,4-dinitro-1-naphthol[18] where the main product isolated was 2-nitro-4-amino-1-naphthol. In a similar manner, the formation of 7-nitro-1-amino-2-naphthol would be expected as the major product from the stannous chloride reduction of 1,7-dinitro-2-naphthol.

Considering group A in Table IV, the relative effect of the nitro group in the α- and β-positions can be clearly seen. The observation that the α-position is the more reactive is consistent with HODGSON's theory[11,20,21] for this difference in positional reactivity. Hodgson considers that the negative inductive effect (—*I*) of the second nucleus must be considered, for, in this manner, the *α*-nitro group will be rendered more electropositive in character than the *β*-nitro group. Furthermore, since it is at the end of a conjugate chain in two of the three resonating structures which naphthalene can assume (Diagram I), it will be more prone to attack by the reducing medium present in acid stannous chloride solutions.

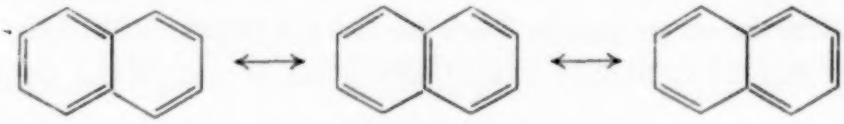

Diagram I

In group B, the effect of two *α*-nitro groups is shown to be equivalent to the reactivity exhibited by *β*-nitronaphthalene. Both compounds in group B are *α*, *α*-dinitronaphthalenes and no intermediate mononitronaphthylamine has been observed during the stannous chloride reductions of these reagents, irrespective as to whether an excess or deficit of reducing agent was used[14]. Only in the catalytic reduction[23,24] selectivity has been experienced. According to Hodgson[11], the two *α*-positions in each of the 1,5- and 1,8-dinitronaphthalenes are identical in situation and are attacked simultaneously by the acid reducing agent to form the respective diamines. This follows from the fact that, even if a deficiency of reducing agent is employed, the surplus dinitronaphthalene is found mixed with the diamine.

The trend of results with the compounds in group C is very similar to the reactivity of the corresponding nitro-naphthol series[7]. This is to be expected when it is realised that the nitroso derivatives are intermediates during the tin reduction of nitro compounds in strongly acid solution[25] (Diagram II).

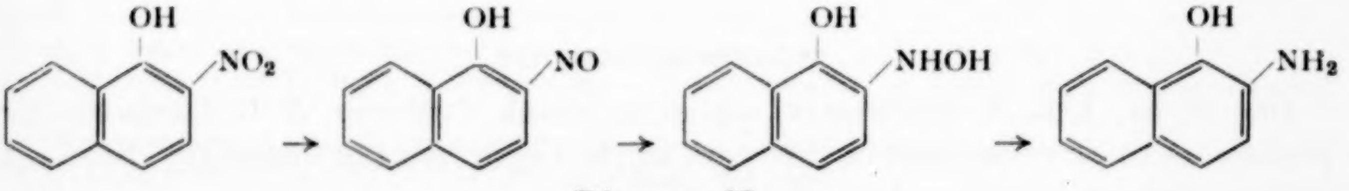

Diagram II

As with the nitronaphthols, a nitroso group in the *β*-position is less reactive than a nitroso group in the corresponding *α*-position, so that 2-nitroso-1-naphthol yields the least intense fluorescence of the four compounds listed, whereas 1-nitroso-2-naphthol is the most reactive reagent. This accentuated difference in positional reactivity in passing from the nitro to nitrosonaphthols could be readily explained if nitroso formation were the rate-determining step in the actual reduction of the nitro group. This is true for the catalytic reduction of nitro groups[23,24], but equivalent data is not yet complete for acid stannous tin reductions, although present indications[12,25-27] are that the same result will be achieved in the latter case.

In Group D, the behaviour of the dinitro compounds, especially the naphthol derivatives, is very similar to that of the parent nitronaphthols. The presence of a second nitro group in the naphthalene nucleus tends to quench the intensity of the fluorescence, so that *α, β*-dinitronaphthols yield a less intense fluorescence than the corresponding *α*- or *β*-mononitronaphthols. In this respect, the compounds in this group are similar in behaviour to the compounds in Group B.

The function of the sulphonic acid group in these reagents is also of interest and is indicated by the comparative properties of 1-nitroso-2-naphthol and 1-nitroso-2-naphthol-3,6-disulphonic acid in Group C. Both exhibit the same reactivity in test, a result which is to be expected in view of the postulate[5] that the function of the sulphonic acid group is essentially one of solvolysis of the parent compound towards polar solvents.

With Group E, the marked difference in reactivity between 2-iodo-4-nitro-1-naphthylamine and 4-chloro-2-nitro-1-naphthylamine is difficult to interpret without a more detailed knowledge of the actual influence of substituents on the reactivity of aromatic systems. In particular, the evaluation of the relative properties of the two compounds in Group E is more complicated than with the compounds in the Groups (A to D) due to the difficulty associated with the estimation of the relative inductive and mesomeric effects in these two systems. It is hoped to clarify this point when the results of an investigation at present being performed in this field, are available[28].

In conclusion, it may be said that any naphthalene compounds containing a nitro group would appear to be potential fluorimetric reagents for stannous tin. The potency of such reagents in this spot test will depend largely on the polar nature of other substituents. Such factors as hydrogen bonding involving the nitro group will impair the ease of reduction and consequently, the sensitivity of the reagent in test. Until more results of research into the relative effects of the inductive and mesomeric moments in naphthalene derivatives are available, it does not appear possible at this time to predict, on theoretical grounds, the structure of a nitronaphthalene derivative which will yield maximum sensitivity of analytical test with stannous tin.

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SUMMARY

Fourteen substituted nitronaphthalene derivatives have been examined as reagents for the fluorimetric detection of tin. The compounds investigated included dinitronaphthalenes, dinitronaphthylamines, halogen substituted mononitronaphthylamines, mononitroso- and dinitronaphthols and their sulphonic acid derivatives. Four of these reagents have been found to exhibit strong fluorescence and another four to give moderate fluorescence with stannous tin. All reagents are capable of detecting 10^{-4} g stannous tin and with four of them, 10^{-5} g is capable of detection in 0.01 ml of solution. The results indicate that two of the most important factors relating structure of reagent to intensity of fluorescence are (a) the position of the nitro group in the naphthalene nucleus, *i.e.*, whether it is *α*- or *β*- or whether it is sterically hindered and (b) the electropositive or electronegative character of *other* substituent groups in the reagent.

RÉSUMÉ

Quatorze dérivés de substitution du nitronaphtalène ont été examinés en vue de leur utilisation comme réactifs fluorimétriques pour l'identification de l'étain. Les résultats obtenus montrent que l'intensité de la fluorescence dépend principalement des deux facteurs suivants: (a) la position du groupe nitro dans le naphtalène; (b) le caractère électropositif ou électronégatif des autres groupes substitués.

ZUSAMMENFASSUNG

14 substituierte Nitronaphthaline wurden auf ihre Eignung als fluorimetrisches Reagenz zum Nachweis von Zinn untersucht. Es konnte gezeigt werden, dass die Intensität der Fluoreszenz von 2 Faktoren bestimmt wird: 1. von der Stellung der Nitrogruppe (α oder β). 2. dem elektro-positiven oder elektro-negativen Charakter der anderen Substituenten.

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A NEW CRYOSCOPIC MICRO-METHOD FOR THE DETERMINATION OF MOLECULAR WEIGHTS

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INTRODUCTION

The known cryoscopic methods for the determination of molecular weights are based on the determination of initial freezing or final melting points. These methods may give reliable results if solute and solvent form no solid solutions, the heat of dilution is negligible and solid and liquid are physically stable near the melting point. But there is little or no information given as to whether these conditions are fulfilled or not.

The method described in this paper is based on the determination of a temperature–heat content curve (melting curve). This curve permits the calculation of molecular weights even when *mixed crystals* occur and the heat of dilution is not negligible. Further, it yields information as to whether the various equilibrium conditions are sufficiently approached.

The method permits extrapolation to infinite dilution and is less open to experimental errors than the known methods.

The determination of a temperature-heat content curve presents no serious difficulty. With the aid of a simple apparatus[1] the curve can be obtained within two hours. Only 200–300 mg of solvent and 1–3 mg of solute are required.

Briefly, the method is as follows. A heating curve permits the determination of the equilibrium temperature of solid and liquid as a function of the fraction of heat of melting consumed. This fraction is nearly equal to the fraction which is molten. (This approximation is not actually introduced in our theoretical considerations and serves only for the preliminary picture.)

The substance of which the molecular weight is to be determined is distributed between the solid and the liquid phase of the solvent. (When no mixed crystals occur the solute is entirely dissolved in the liquid phase of the solvent.)

As the melting proceeds a series of concentrations of the solute and the pertaining depressions is obtained. This series permits extrapolation to zero concentration.

As will be shown in the theoretical part it is more exact to plot amounts of heat consumed as a function of the depression.

THEORETICAL PART

The molecules of a polar substance when dissolved in a solvent may show a strong tendency to mutual association. This mutual association may be largely prevented when solvents showing association with the solute are applied. Association with the *excess* solvent hardly effects the molecular ratio of solvent and solute; moreover its effect on the depression of the melting point may be eliminated by extrapolation to infinite dilution. However, when (owing to the choice of the solvent) mutual association of the solute may be neglected, heats of dilution (owing to solute-solvent interaction) may be important and have to be accounted for.

Therefore the following equation is used as a starting-point for further considerations:

$$\int_{T_O}^{T_S} \frac{Q}{T^2}\,\mathrm{d}T - \int_{T_O}^{T_S} \frac{\Delta \overline{W}_L}{T^2}\,\mathrm{d}T + \int_{T_O}^{T_S} \frac{\Delta \overline{W}_S}{T^2}\,\mathrm{d}T = R \ln(1 - X_L) - R \ln(1 - X_S) \quad (1)$$

where Q = molar heat of melting of pure solvent at any temperature; Q_O = molar heat of melting of pure solvent at the melting point; ΔW_L and ΔW_S = partial molar heats of dilution of the liquid and the solid phase, respectively; T_S = any temperature where liquid and solid are in equilibrium (°K); T_O = melting temperature of pure solvent (°K); $\Delta T = T_S - T_O$; X_L, X_S = mol fraction of solute in the liquid and solid phase respectively; ΔC_P = difference of molar specific heats of liquid and solid phase; R = gas constant.

Assuming that $Q = Q_O + \Delta C_p \Delta T$ and that ΔW_L and ΔW_S do not depend on temperature, equation (1) may be integrated:

$$\frac{Q_O + \Delta \overline{W}_L - \Delta \overline{W}_S}{T_O T_S}\,\Delta T + \frac{\Delta C_P}{2 T_S^2}(\Delta T)^2 = R \ln\left(\frac{1 - X_L}{1 - X_S}\right) \quad (2)$$

At low and moderate values of X_L and X_S, equation (2) can be simplified to:

$$\frac{Q_O + \Delta \overline{W}_L - \Delta \overline{W}_S}{T_O T_S}\,\Delta T + \frac{\Delta C_P}{2 T_S^2}(\Delta T)^2 = -R(X_L - X_S) \quad (3)$$

This approximation introduces an error not exceeding 1.5% at the maximum concentrations* ($X_L < 0.03$) applied in this method; moreover, extrapolation to zero concentration largely eliminates this error.

Suppose that from a sample with a total concentration X, a mol fraction y has been melted.

Thus,

$$y X_L + (1 - y) X_S = X \text{ and } (X_L - X_S) = \frac{X - X_S}{y}$$

Substituting this in equation (3) yields

$$\frac{y(Q_O + \Delta \overline{W}_L - \Delta \overline{W}_S)_y}{T_O T_S}\,\Delta T + \frac{y\,\Delta C_P (\Delta T)^2}{2 T_S^2} = -R(X - X_S) \quad (4)$$

---

* X is limited to about 0.003. $X_S < X$ unless elevation of the melting point occurs. The smallest fraction molten that is considered amounts to 10%, thus $X_L \leqslant 10\,X$.

When a mol fraction y has been melted the fraction of the total heat of melting supplied, f_y, is approximately equal to

$$\frac{y(Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S)_y}{(Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S)_{y-1}}$$

(At $y = 1$ the approximation is complete).

Substituting the approximate value of f_y in equation 4 results in:

$$f_y\,\Delta T + \frac{y\,\Delta C_P(\Delta T)^2\,T_O T_S}{2T_S^2(Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S)_{y-1}} = \frac{R(X - X_S)T_O T_S}{(Q_O + \Delta\overline{W}_L - \Delta\overline{W}_S)_{y-1}} \quad \ldots\ldots (5)$$

Equation (5) contains no variable values of ΔW_L and ΔW_S which may become important at large values of X_L.

When the solvents used have a heat of fusion of about 4000 cal/mol and $X < 0.003$, $(\Delta W_L - \Delta W_S)_{y-1}$ can certainly be neglected. If only the range $0.1 < y < 1$ is considered and if ΔC_p is assumed equal to 3R or 6 cal/mol, the correction containing ΔC_p may be estimated at about 0.2% of $f_y \Delta T$. Moreover this correction term approaches zero when extrapolation to $\Delta T = 0$ is made.

Therefore it is permissible to simplify equation (5) to:

$$f_y\,\Delta T = -\frac{RT_O T_S}{Q_O}(X - X_S) \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Now, in many cases X_S appears to be a linear function of the temperature at low values of X_S ($X_S < X$) so that $X_S = k\Delta T$.

Substitution in (6) yields

$$f_y\,\Delta T = -\frac{RT_O T_S}{Q_O}X + \frac{kRT_O T_S}{Q_O}\Delta T \quad \ldots\ldots\ldots\ldots\ldots (7)$$

According to equation (7) a determination of a molecular weight may be performed in the following way.

A temperature–heat content curve (melting curve) of a solvent containing about 0.003 mol solute per mol is determined.

Corresponding values of f_y and ΔT are evaluated from the melting curve. Then $f_y\Delta T$ is plotted as a function of ΔT. According to equation (7) this plot should be an approximately straight line. When extrapolated to $\Delta T = 0$ the ordinate is intersected at

$$(f_y\,\Delta T)_{\Delta T=0} = -\frac{RT_O^2}{Q_O}X$$

The angle of intersection is determined by $\dfrac{kRT_O^2}{Q_O}$

The value of $(f_y\Delta T)_{\Delta T=0}$ being known, the molecular weight of the solute may be calculated (see "experimental procedure").

EXPERIMENTAL PROCEDURE

Apparatus

The apparatus for the determination of temperature-heat content curves[1,2] permits a constant amount of heat per unit time to be supplied to the sample. The rate of heating of the solid is chosen as 0.2–0.6°/min. Under the prevailing conditions the melting process takes about 60 min. The temperature is recorded from 20° below the melting point of the solvent up to about 5° above the melting point.

The thermometers used are shortened stem thermometers with a range of at least 50° subdivided in 0.1°, so that readings can be taken with an accuracy of ± 0.01°. Temperature readings are taken at intervals of 1 min.

For further details concerning the determination of temperature–heat content curves reference is made to the literature[1,2].

Preparation of the sample

1–3 mg of substance (depending on the molecular weight is weighed in the measuring vessel[1]. A weighed amount of about 300 mg of solvent is added. Then the sample is heated to 5–10° above the melting point of the solvent and stirred thoroughly until the substance has completely dissolved.

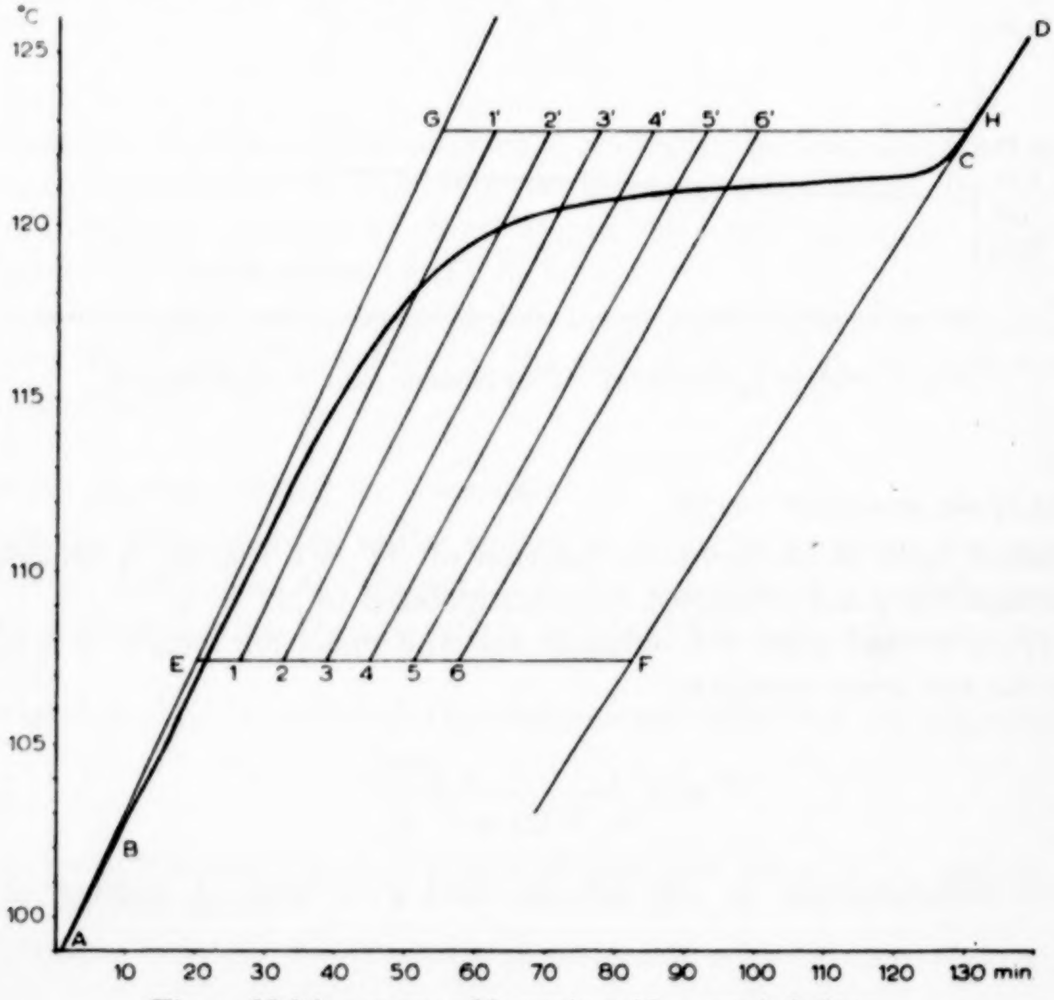

Fig. 1. Melting curve of benzoic acid + naphthalene.

The solution obtained is cooled rapidly. In order to prevent segregation, solidification should be completed within two min.

To eliminate crystal imperfections the sample is kept for 30 min at about 10° below the melting point. The sample is then ready for the determination of a melting curve.

Evaluation of f_y and ΔT

Melting curves of both the sample and the pure solvent are determined.

The general appearance of a melting curve is shown in Fig. 1. The section A B represents the heating of the solid (and the measuring vessel). At B the process of melting starts and it is completed at C. The straight line C D represents the heating of the molten sample. The amount of heat consumed between B and C is the sum of the heat of fusion, and the amounts of specific heat consumed between B and C.

The equivalent of the total heat of fusion at a certain temperature is found by extrapolating the lines A B and C D at the temperature desired The temperatures corresponding to distinct values of f_y are derived in the following way: the lines E F and G H are drawn and each line is divided into ten equal fractions. The lines 1–1′, 2–2′, 3–3′ etc. are drawn. The temperature at which the line 1–1′ intersects the melting curve corresponds to $f_y = 0.1$, the intersection of 2–2′ corresponds to $f_y = 0.2$ etc.

The difference ΔT of the temperatures of the pure solvent and the solution at the same value of f_y is determined.

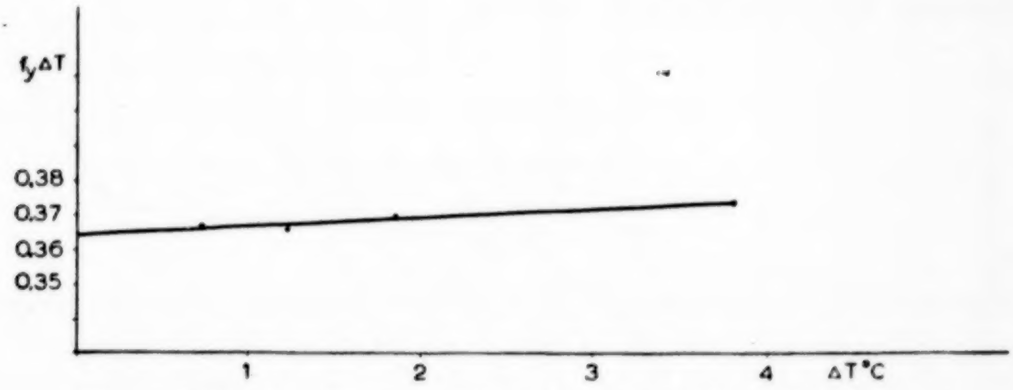

Fig. 2. Plot of $f_y\Delta T$ *versus* ΔT of benzoic acid + naphthalene.

Calculation of the molecular weight

The product $f_y\Delta T$ is plotted as a function of ΔT (see Fig. 2). A straight line is drawn through the points obtained and extrapolated to $\Delta T = 0$.

$(f_y\Delta T)_{\Delta T=0}$ is read from the ordinate and the molecular weight m is calculated according the following equation:

$$m = \frac{1}{(f_y\Delta T)_{\Delta T=0}} \cdot \frac{gRT_0^2}{q}$$

where g = concentration in g/g solvent, and q = heat of melting of solvent per g.

NOTES

Correction for eutectic melting

If the melting curve shows an isothermal part owing to the melting of the eutecticum the following procedure is advisable. First $f_y\Delta T$ is determined in the ordinary way at $f_y = 0.5$. (When the isothermal process is still present near $f_y = 0.5$ a new melting curve should be determined with a sample containing less solute.) Then $\Delta T'$ is determined at a temperature T' slightly higher than the eutectic temperature.

The value of f_y' corresponding to $\Delta T'$ is calculated:

$$f'_y = \frac{(f_y\ \Delta T)_{y=0.5}}{\Delta T'}$$

A horizontal line through T' is drawn. On this line two fixed values of f_y' occur *viz.* f_y' (at the intersection with the melting curve) and $f_y = 1$ (at the intersection with CD).

With the aid of these two points a point is determined where f_y should be equal to zero. Through this point a new line A′B′ is drawn parallel to AB. The curve is now further treated as if A′B′ actually represented the heating of the solid. This yields a new series of values of f_y which is considered as the correct one.

If the curve shows no isothermal part it may be assumed that the eutectic melting occurs below the starting temperature. Yet the heat consumed before the first recording of temperature must be corrected for. At the lowest temperature recorded (say $\Delta T' = 20°$) a fixed value f_y' is determined by

$$f'_y = \frac{(f_y\ \Delta T)_{y=0.5}}{\Delta T'}$$

The correction procedure then followed is analogous to that described above. The correction thus introduced is relatively small (about 1%). When the correction is omitted it introduces an error of about 1% in the found molecular weight; this is not eliminated by extrapolation to $\Delta T = 0$.

When mixed crystals occur the correction is not permissible. Thus in the rare cases where a very slight partial miscibility in the solid phase occurs, an error of about 1% may be introduced.

Correction for emergent stem of the thermometer

Although the determination of the molecular weight is based on the measurement of temperature differences, the correction for the emergent stem of the thermometer can not be neglected when the cryoscopic constant has been calculated from calorimetric data.

The correction Δ to be added to the temperature difference ΔT amounts to

$$\Delta = 1.6(t_2 + t_3 - t_1)\Delta T \cdot 10^{-4}\,{}^{\circ}\mathrm{C}$$

where t_1 = room temperature, t_2 = length of emergent stem in °C, and t_3 = melting point of the solvent in °C.

If for example, benzoic acid is used this correction may be more than 1%.

Solid solutions

When solid solutions occur equilibrium between solid and liquid is less easily approached owing to low diffusion rates in the solid phase. Lack of equilibration was found during the determination of the molecular weight of phenanthrene with diphenyl as solvent. In the first determination the plot of $f_y\Delta T$ *versus* ΔT deviated strongly from a straight line. During a second experiment heat was supplied at intervals and the sample was kept under adiabatic conditions for a sufficiently long time after each supply of heat. The plot was then a straight line and the correct molecular weight was found.

Solvents used

Preferably solvents are used which melt within 0.1° between $f_y = 0.1$ and $f_y = 0.5$ and which have a heat of melting of about 4000 cal/mol.

Succesfully applied solvents were:
benzoic acid (m.p. 122.4°, heat of melting 33.9 cal/g) diphenyl (m.p. 69.0°, heat of melting 28.8 cal/g) phenylacetic acid (m.p. 77°, heat of melting 41.2 cal/g) tetrachlorobenzene (m.p. 140°, heat of melting 27.1 cal/g).

Other solvents may also be useful. Solvents showing polymorphism near the melting point should be avoided.

EXPERIMENTAL RESULTS

Tables I and II show results of molecular weight determinations in benzoic acid and diphenyl respectively.

TABLE I

Solvent used is benzoic acid

compound	*mol. weight*	*mol. weight found*	*conc. weight %*	*error %*	*system*
naphthalene	128	129	1.0[a]	+0.8	no solid sol.
adipinic acid	146	146	0.6[a]	0	no solid sol.
diphenyl	154	155	1.0	+0.7	no solid sol.
antipyrine	188	187	0.6	—0.5	no solid sol.
antraquinone	208	207	0.4	—0.5	no solid sol.
tetraphenylethane	334	336	0.6	+0.6	no solid sol.
k-aglycone[3]	506	507[b]	1.0	+0.2	no solid sol.
bromophenol blue	670	670	1.2	0	no solid sol.
edible fat	864[a]	859	1.1	—0.6	no solid sol.

[a] determined by titration.
[b] mean of two determinations differing respectively +1% and —1% from the correct value.

TABLE II

Solvent used is diphenyl

compound	*mol. weight*	*mol. weight found*	*conc. weight %*	*error %*	*system*
phenanthrene	178	180	1.2	+1.1	solid sol.
anthraquinone	208	208	0.5	0	no solid sol.
edible fat	864	857	1.0	+0.8	no solid sol.

In some of the determinations mentioned in Table I the actual concentration of the solute taken is more than 3 mol %, nevertheless the error in the results is smaller than 1%.

A preliminary investigation has been made concerning the application of the method to polymers. So far, it has not been possible to obtain high polymers with known molecular weights. We restricted our investigation to polymers of the polyester type with molecular weights up to 2000. The molecular weights found tallied with those determined by a chemical method. Dependent on the degree of polymerization, solutions of polymers show deviations from equation (7).

FLORY[4] and HUGGINS[5] discussed the influence of interaction on the activity of polymers. With the aid of the method described in this paper heats of dilution are accounted for. Since the method gives a series of data pertaining to different concentrations, it provides an easy means of discerning other effects of interaction and it may be possible to determine entropy effects arising from the dilution of a polymer solution.

In case the entropy effects are important a simple linear extrapolation to zero concentration is not permissible. Development of a suitable extrapolation method will be a matter of further investigation.

Discussion

The results presented above have not been selected and were obtained by a single experiment unless stated otherwise. The deviations from the theoretical molecular weight never exceeded 1% when no solid solutions were present.

The molecular weight determination of phenanthrene in diphenyl, which showed a rather large miscibility in the solid phase, deviated only 1.1%. If another cryoscopic method had been applied to the same system, the error would have been 50%. A determination of the molecular weight of benzoic acid in diphenyl failed. The plot of $f_y \Delta T$ *versus* ΔT showed a strong curvature and the values of $f_y \Delta T$ corresponded to nearly twice the theoretical molecular weight. With phenylacetic acid as solvent the correct molecular weight of benzoic acid was found. This experience illustrates the views presented in the theoretical part, *viz.* a solute-solvent association may prevent mutual association of the molecules of the solute.

With respect to the known cryoscopic methods the determination of melting curves has the following advantages. Owing to the fact that heat fractions are determined the influence of the heats of dilution is minimized. Polymorphic behaviour of the solvent which may cause unknown deviations in the heat of melting and in the cryoscopic constant may be recognized. Although the method is a micro method it is not based on the inaccurate micro-melting point determination and consequently solvents with a large cryoscopic constant (small heat of melting) are not required.

ACKNOWLEDGEMENT

We wish to thank the director of the Institute for Cellulose Research of the A.K.U. for providing us with some polymer samples of which the molecular weight had been determined by chemical means in his Institute.

SUMMARY

A method is described for molecular weight determination based on a temperature–heat content curve. About 2 mg of substance is required. The method is applicable even when solute and solvent form mixed crystals. A wide variety of solvents may be used. The method may yield good results in the polymer field.

The accuracy obtained is better than 1%. The new method appears to be more reliable and accurate than known cryoscopic methods.

RÉSUMÉ

Une méthode cryoscopique est proposée pour la détermination des poids moléculaires; elle est basée sur la courbe température–enthalphie, fournie par un appareil simple.

Cette méthode permet une accuratesse de 1% obtenue avec des échantillons de 2 mg environ.

ZUSAMMENFASSUNG

Es wird eine kryoskopische mikro Methode (Substanz Menge etwa 2 mg) zur Bestimmung von Molekulargewichten beschrieben, die auf der Aufstellung und Auswertung von Schmelzkurven beruht. Die Genauigkeit der Methode beträgt 1%.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

III[1]. THE IMPORTANCE OF THE IONISATION OF THE WEAK ACID OR BASE IN BUFFER MEDIA CALCULATIONS

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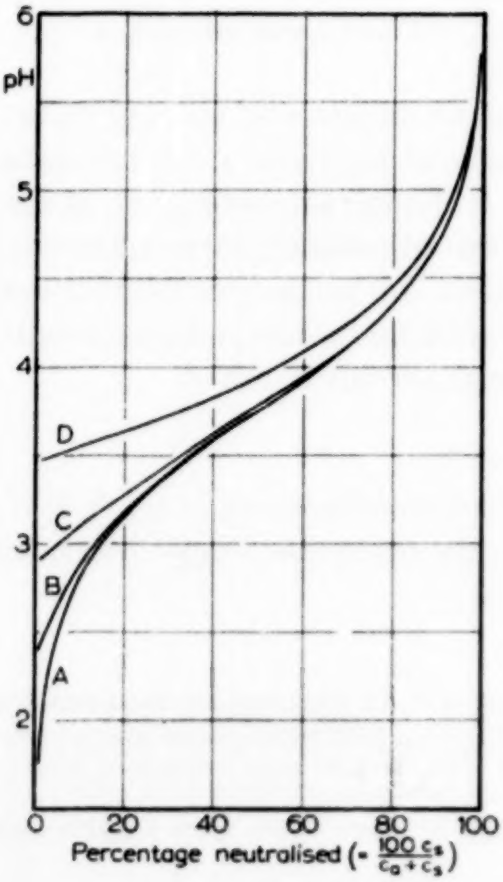

Fig. 1. pH of formic acid – formate buffer solutions: $K_a = 1.76 \cdot 10^{-4}$. Curve A: calculated from the simple equation (1). Curves B to D: calculated from the exact cubic equation[3]:

$$[H^+]^3 + (c_s + K_a)[H^+]^2 - (K_w + K_a c_a)[H^+] - K_a K_w = 0$$

Buffer concentration ($c_a + c_s$) in Curve B, 0.1 M; in Curve C, 0.01 M; in Curve D, 0.001 M.

When buffer solutions prepared to give a specific pH value are checked by measurement, it often happens that the measured pH differs from the expected pH[2], being greater with acid buffers and less with basic buffers than expected, and the difference increases with increasing dilution of the solution and with increasing ionisation constant of the weak acid or base. Similar discrepancies arise in comparing theoretical and experimental titration curves involving weak and strong components. Study of such phenomena reveals that hydrogen ion buffers are invariably more efficient in resisting change of pH than is expected (Fig. 1). The discrepancies arise because the assumptions upon which the derivation of the simple buffer equations in common use are based are no longer valid. Whilst it is generally realised that corrections have to be applied to these equations when working at extremes of the buffer range, it is not generally appreciated how severe are the limitations, particularly in respect to ionisation of the weak acid or base, of the simple equations.

In the case of *acid buffers*, derivation of the simple equation (1) assumes that the concentration of anions furnished by the salt, of concentration c_s, adequately suppresses ionisation of the weak acid, so that the concentration of HA can be written equal to c_a the total concentration of acid present. When this assumption is no longer valid, the ionisation of the weak acid can be taken into account[3] by use of the more precise quadratic equation (2).

$$[H^+] = \frac{c_a}{c_s} K_a \qquad (1)$$

$$[H^+] = \tfrac{1}{2}\left[\left\{(c_s + K_a)^2 + 4\,K_a c_a\right\}^{\frac{1}{2}} - (c_s + K_a)\right] \qquad (2)$$

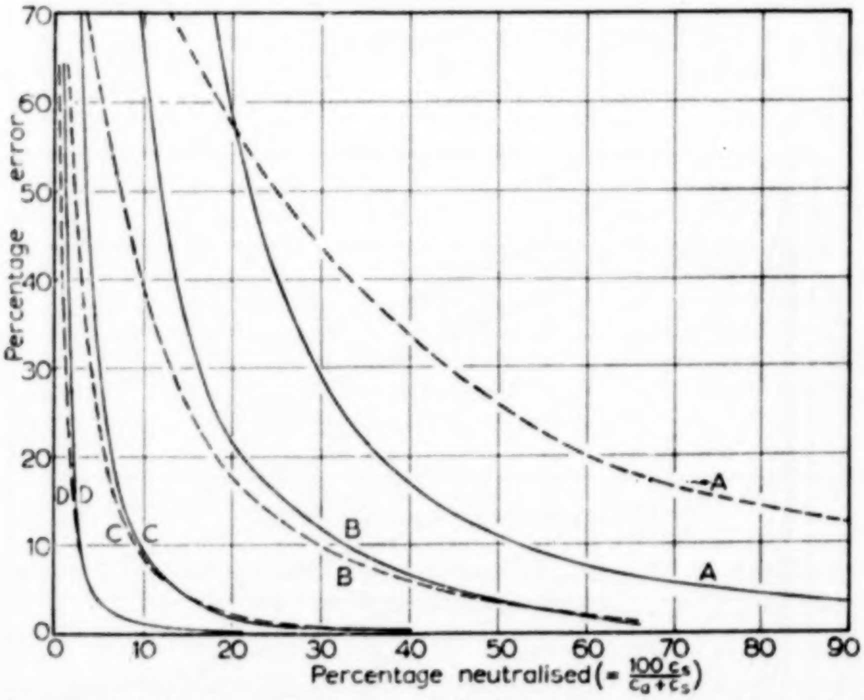

Fig. 2. The error incurred in buffer solution calculations by ignoring the ionisation of the weak acid or weak base. Full lines: acid buffers. Broken lines: basic buffers.

Curves A		Curves B	
Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b	Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b
10^{-1}	1.0 *M*	10^{-2}	1.0 *M*
10^{-2}	0.1 *M*	10^{-3}	0.1 *M*
10^{-3}	0.01 *M*	10^{-4}	0.01 *M*
10^{-4}	0.001 *M*	10^{-5}	0.001 *M*

Curves C		Curves D	
Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b	Ionisation constant K_a or K_b	Total buffer concentration $c_s + c_a$ or c_b
10^{-3}	1.0 *M*	10^{-4}	1.0 *M*
10^{-4}	0.1 *M*	10^{-5}	0.1 *M*
10^{-5}	0.01 *M*	10^{-6}	0.01 *M*
10^{-6}	0.001 *M*	10^{-7}	0.001 *M*

The relative error E incurred by the use of the simple equation is then given by

$$E = \frac{\text{simple value of } [\mathrm{H^+}] - \text{corrected value of } [\mathrm{H^+}]}{\text{corrected value of } [\mathrm{H^+}]} \quad \ldots\ldots\ldots \quad (3)$$

from which the percentage error is obtained by multiplication by 100.

Substitution of the values from (1) and (2) in (3) gives the master discriminant[1] (4),

$$c_aK_a + c_sK_a(1 + E) - Ec_s^2(1 + E) = 0 \quad \ldots\ldots\ldots \quad (4)$$

Solution of the master discriminant for E[1] gives the results shown in Fig. 2, indicating that the error rises sharply as the ionisation constant K_a increases above 10^{-7} and as the concentration of the buffer solution falls.

For *basic buffers*, the effect is even more pronounced. In this case the simple equation (5) is

$$[\mathrm{H^+}] = \frac{c_s\, K_w}{c_b\, K_b} \quad \ldots\ldots\ldots \quad (5)$$

Corrected for ionisation of the weak base[3], this becomes

$$[\mathrm{H^+}] = \frac{1}{2c_bK_b}\left[K_w(K_b + c_s) + \left\{K_w^2(K_b + c_s)^2 + 4K_bc_bK_w^2\right\}^{\frac{1}{2}}\right] \quad \ldots\ldots \quad (6)$$

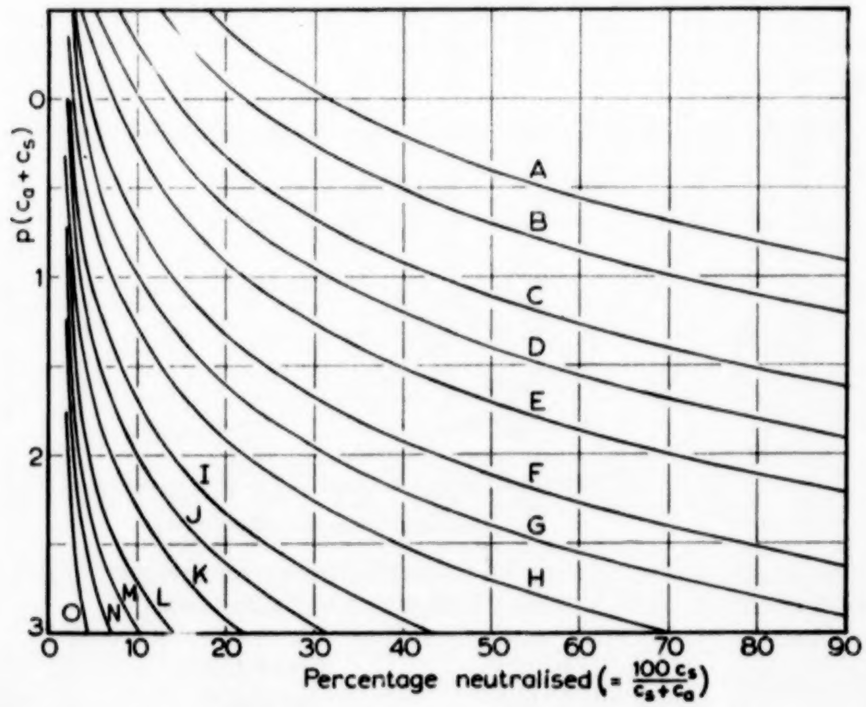

Fig. 3. The relationship between total buffer concentration and degree of neutralisation for given errors and ionisation constants.

Curve A, $K = 10^{-3}$, error = 1%
Curve B, $K = 10^{-3}$, error = 2%
Curve C, $K = 10^{-3}$, error = 5%
Curve D, $K = 10^{-4}$, error = 1%
Curve E, $K = 10^{-4}$, error = 2%
Curve F, $K = 10^{-4}$, error = 5%

Curve G, $K = 10^{-5}$, error = 1%
Curve H, $K = 10^{-5}$, error = 2%
Curve I, $K = 10^{-5}$, error = 5%
Curve J, $K = 10^{-6}$, error = 1%
Curve K, $K = 10^{-6}$, error = 2%
Curve L, $K = 10^{-6}$, error = 5%

Curve M, $K = 10^{-7}$, error = 1%
Curve N, $K = 10^{-7}$, error = 2%
Curve O, $K = 10^{-7}$, error = 5%

and the master discriminant[1] is

$$Ec_s^2 + (1 + E)c_sK_b + (1 + E)^2c_bK_b = 0 \quad \ldots\ldots\ldots\ldots (7)$$

which on solution for E^1 gives the results included in Fig. 2.

Examination of Fig. 2 shows that quite serious errors can arise through neglect of the ionisation of the weak acid or base. Indeed, if the maximum permissible relative error is E, the simple equations are completely invalid when the ionisation constant of acid or base exceeds Ec_s. In calculating the pH of buffer media, it is therefore necessary to consider whether correction for ionisation of the weak acid or base will make a significant difference, particularly when the ionisation constant exceeds 10^{-7} and the total buffer concentration is less than 0.1 M. This is particularly the case when dealing with media in which the acid concentration exceeds the salt concentration and in the calculations for displacement titrations.

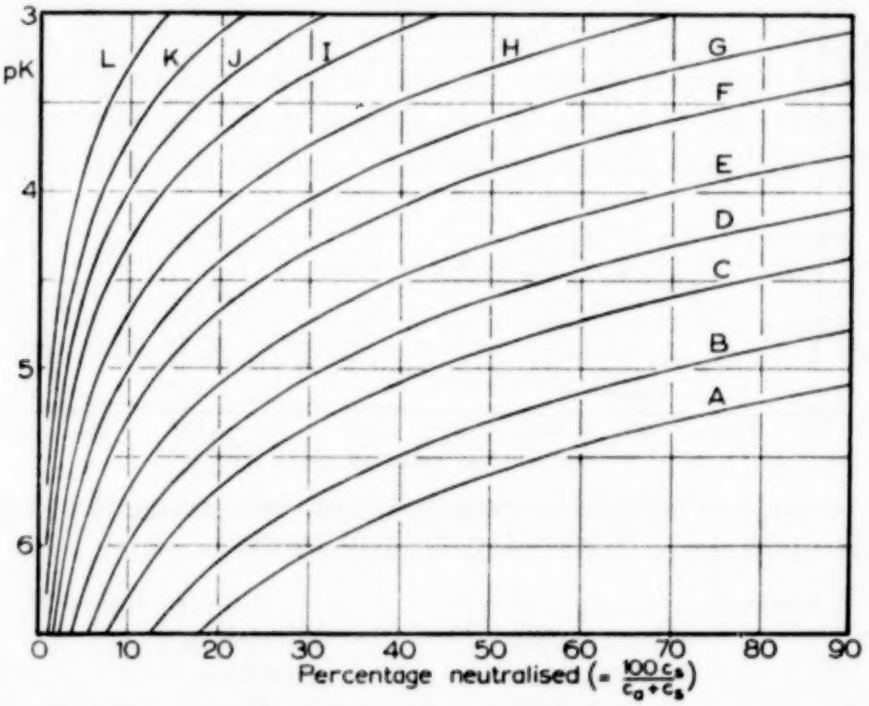

Fig. 4. The relationship between ionisation constant and degree of neutralisation for given errors and buffer concentrations.

Curve A, $c_a + c_s = 0.001$ M, error = 1%
Curve B, $c_a + c_s = 0.001$ M, error = 2%
Curve C, $c_a + c_s = 0.001$ M, error = 5%

Curve D, $c_a + c_s = 0.01$ M, error = 1%
Curve E, $c_a + c_s = 0.01$ M, error = 2%
Curve F, $c_a + c_s = 0.01$ M, error = 5%

Curve G, $c_a + c_s = 0.1$ M, error = 1%
Curve H, $c_a + c_s = 0.1$ M, error = 2%
Curve I, $c_a + c_s = 0.1$ M, error = 5%

Curve J, $c_a + c_s = 1.0$ M, error = 1%
Curve K, $c_a + c_s = 1.0$ M, error = 2%
Curve L, $c_a + c_s = 1.0$ M, error = 5%

To facilitate the assessment of conditions under which such correction becomes necessary, data calculated from particular discriminants[1] derived from the master discriminants (4) and (7) are presented in graphical form in Figs. 3 and 4, in which the degree of neutralisation is related to total buffer concentration for various values of ionisation constant and allowable error, or to ionisation exponent for various total buffer concentrations and allowable errors.

In Fig. 3, the area above a particular curve defines the conditions under which the simple equation (1) is valid. For example, if the total buffer concentration is 0.1 M, and the permissible error is 2%, then if the weak acid has an ionisation constant of 10^{-4} the simple equation is valid when more than 22.5% of the acid has been neutralised (*i.e.* $c_a/c_s \leqslant 3.45$). Similarly, if the ionisation constant is 10^{-5}, the permissible error is 1% and equal amounts of acid and salt are present (*i.e.*, 50% neutralised) then the simple equation is valid if the total buffer concentration exceeds 0.004 *M*. In Fig. 4, the area below a particular curve defines the conditions under which the simple equation is valid. For example, if equal amounts of acid and salt are present, the total concentration is 0.01 *M* and the permissible error is 2%, then the

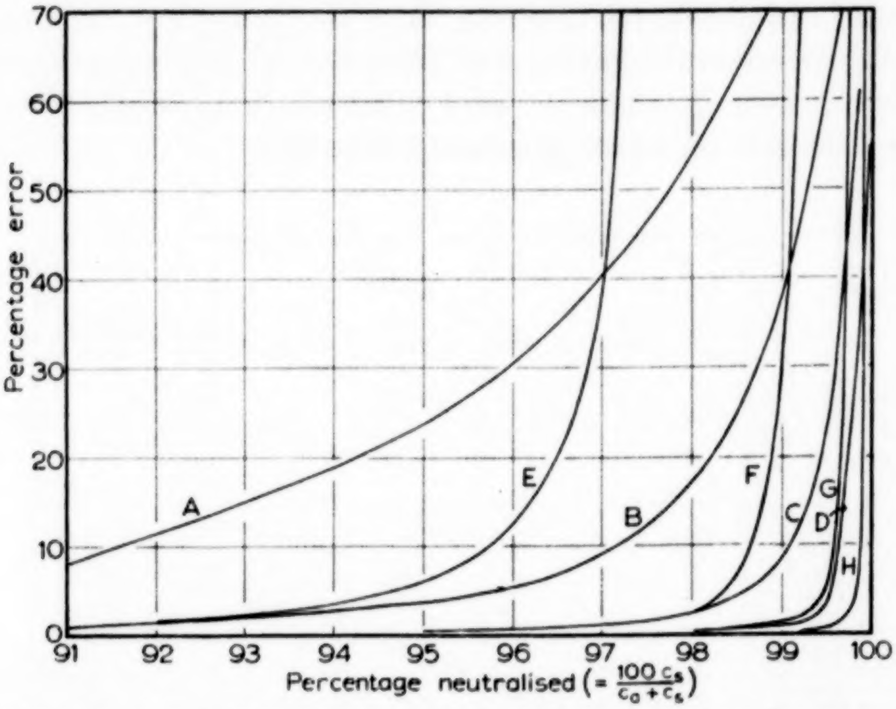

Fig. 5. The error incurred in buffer solution calculations by ignoring the hydrolysis of the salt Curves A to D: acid buffers.

Curve A

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-11}	1.0 *M*
10^{-10}	0.1 *M*
10^{-9}	0.01 *M*
10^{-8}	0.001 *M*

Curve B

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-10}	1.0 *M*
10^{-9}	0.1 *M*
10^{-8}	0.01 *M*
10^{-7}	0.001 *M*

Curve C

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-9}	1.0 *M*
10^{-8}	0.1 *M*
10^{-7}	0.01 *M*
10^{-6}	0.001 *M*

Curve D

Ionisation constant K_a	Total buffer concentration $c_s + c_a$
10^{-8}	1.0 *M*
10^{-7}	0.1 *M*
10^{-6}	0.01 *M*
10^{-5}	0.001 *M*

Curves E to H: basic buffers. Total buffer concentration, $c_s + c_a = 0.1$ *M*.

E, $K_b = 10^{-9}$; F, $K_b = 10^{-8}$; G, $K_b = 10^{-7}$; H, $K_b = 10^{-6}$.

Note: In the case of basic buffers, the progression is different from that in the other sets of curves shown. As the buffer concentration falls, the error increases so rapidly that for constants less than 10^{-7}, and buffer concentrations less than 0.1 *M*, the curves could not be illustrated even on a 0–100 percentage neutralised ordinate. Curves for only a single concentration are therefore given.

simple equation is valid when the ionisation constant of the acid is less than $5 \cdot 10^{-5}$. Similarly, for an acid of ionisation constant 10^{-5}, a total buffer concentration of 0.01 M and an error of 1%, more than 31.5% of the acid must be neutralised before the simple equation becomes valid.

Although the particular discriminants[1] for basic buffers[1] differ from those for acid buffer, the difference is small, and the curves in Figs. 3 and 4 will serve equally well for basic buffers.

Calculation of titration curves

Disturbances due to ionisation of the weak acid or base are important in buffer solution and displacement titration calculations, but unless the ionisation constant exceeds about 10^{-4}, this effect is not important in calculations for ordinary acid-base titrations. In the region of particular interest in the immediate vicinity of the equivalence point, it is the second assumption made in deriving equations (1) and (5) which breaks down, *viz.*, that loss of anions of weak acid or of cations of weak base by hydrolysis is so small that the anion or cation concentration can be written equal to the total salt concentration c_s. In this case, loss of anions in acid buffers can be taken into account[3] by use of the quadratic equation (8) embodying the hydrolysis correction,

$$[\mathrm{H}^+] = \frac{1}{2c_s}\left[\left\{(c_aK_a + K_w)^2 + 4K_aK_wc_s\right\}^{\frac{1}{2}} + (c_aK_a + K_w)\right] \quad \ldots\ldots \quad (8)$$

By substitution of the values from (1) and (8) in (3), the master discriminant (9) follows,

$$(1 - E)^2c_sK_w + (1 - E)c_aK_w - Ec_a^2K_a = 0 \quad \ldots\ldots\ldots\ldots \quad (9)$$

solution of which for E^1 gives the results shown in Fig. 5.

In the case of basic buffers, correction for loss of cation by hydrolysis[3] gives,

$$[\mathrm{H}^+] = \frac{1}{2K_b}\left[\left\{(K_bc_b + K_w)^2 + 4K_wK_bc_s\right\}^{\frac{1}{2}} - (K_bc_b + K_w)\right] \quad \ldots\ldots \quad (10)$$

From (5) and (10), the master discriminant (11) follows,

$$E(1 + E)K_bc_b^2 - (1 + E)K_wc_b - c_sK_w = 0 \quad \ldots\ldots\ldots\ldots \quad (11)$$

which, on solution for E^1 gives the results included in Fig. 5.

Study of Fig. 5 shows that this effect, though profound in the equivalence point region of titrations, does not extend far into the range of buffer solutions except at high dilution and very low ionisation constants, such as are not common in practice.

CONCLUSIONS

Though equations (1) and (5) indicate that the pH values of buffer solutions are independent of absolute concentration and should not alter on dilution, the effects of ionisation of the weak acid or base and of hydrolysis of the salt are strongly concentration dependent, and where these come into play pH is affected by dilution. Examination of these factors indicates that for best results, buffers should be chosen from acids or bases (better acids to avoid the temperature dependence of basic buffers on K_w) whose ionisation constant lies between 10^{-5} and 10^{-8}, and used at concentrations higher than 0.01 M. When stronger acids or bases are necessarily employed, the concentration should be increased still further. Though the buffering effect as measured by the slope of the pH – neutralisation curve increases with decreasing concentration of the solution (*cf.* Fig. 1), this is considerably offset by increasing sensitivity to dilution and decreasing buffer capacity.

ACKNOWLEDGEMENT

Thanks are due to Dr. W. B. JEPSON for his help in checking the mathematics and confirming the conclusions in this study.

SUMMARY

The limitations of the simple expressions for the hydrogen ion concentration of buffer solutions are examined. The necessity for taking into account the ionisation of the weak acid or base is greater than is generally appreciated, and neglect of this factor can lead to surprisingly large errors which increase rapidly on dilution of the solution. Graphical data are presented to facilitate definition of conditions under which this correction becomes necessary.

RÉSUMÉ

L'auteur examine le cas du calcul de la concentration en ions hydrogène des solutions tampon et montre la nécessité de tenir compte de l'ionisation de l'acide ou de la base faible. Négliger ce facteur peut conduire à des erreurs étonnament grandes, augmentant rapidement avec la dilution.

ZUSAMMENFASSUNG

Der Einfluss der Ionisation schwacher Säuren oder Basen bei der Berechnung der Wasserstoffionenkonzentration in Pufferlösungen wurde untersucht. Es hat sich ergeben, dass die Vernachlässigung dieses Faktors beim Verdünnen der Lösungen zu grossen Fehlern führen kann.

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A NEW SPOT TEST FOR PALLADIUM*

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(Received July 25th, 1959)

A new test for palladium is proposed based upon the formation of a stable orange-yellow chelate of palladium(II) with phenyl-α-pyridyl ketoxime[1]. Palladium phenyl-α-pyridyl ketoximate shows maximum light absorption at 410 mμ and the chelate is highly soluble in chloroform. It can be completely extracted in a single pass from the aqueous solution between pH 5 and 11.

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* Presented at the South West Regional Meeting of the A.C.S. at Baton Rouge, La., December 3–5, 1959.

EXPERIMENTAL

Reagent solution

Phenyl-α-pyridyl ketoxime was prepared at this laboratory[1] and a 1% solution of it in 95% ethanol was used as the reagent solution.

Standard palladium solution

The palladium solution was prepared from palladium(II) chloride and was 4 *M* with respect to hydrochloric acid. It was standardized gravimetrically by precipitating palladium with dimethylglyoxime. The solutions for other cations were prepared from their sulfates, nitrate and chlorides.

PROCEDURE

One drop of the weakly acidic or neutral solution is placed into the depression of a white spot plate and is treated with one drop of the reagent solution. When the test solution is strongly acidic, a few drops of 0.5 *M* sodium carbonate solution are added after the addition of the reagent solution. A yellow color indicates the presence of palladium.

Effects of other ions

The following ions do not interfere with the test: Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, NH_4^+, Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, Al^{+3}, Ga^{+2}, Ce^{+3}, Ce^{+4}, Tl^+, Ti^{+4}, Zr^{+4}, Sn^{+2}, Pb^{+2}, Th^{+4}, As^{+3}, Cr^{+3}, Sb^{+3}, Bi^{+3}, Mn^{+2}, Fe^{+3}, BO_2^-, $B_4O_7^{-2}$, SiO_3^{-2}, GeO_3^{-2}, NO_2^-, NO_3^-, HPO_4^{-2}, $S_2O_3^{-2}$, SO_3^{-2}, SO_4^{-2}, SeO_3^{-2}, SeO_4^{-2}, F^-, Cl^-, Br^-, ClO_3^-, ClO_4^-, BrO_3, IO_3^-, MoO_4^{-2}, TeO_3^{-2}, TeO_4^{-2}, WO_4^{-2}, VO_2^{+2}, VO_4^{-2}, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, CNS^-, acetate, oxalate, malonate, succinate, tartrate, citrate, sulfosalicylate, salicylate and formate.

The other platinum metal ions, CrO_4^{-2}, $Fe(CN)_6^{-3}$, MnO_4^-, interfere with the test due to the color of these ions; Hg_2^{+2} and Hg^{+2} interfere due to the precipitation of the black oxide. These interferences can be eliminated by extracting the palladium chelate with chloroform. Copper(II), Fe^{+2}, Co^{+2}, Ni^{+2} also form colored complexes with the reagent, soluble in chloroform. Their interference is prevented by masking with EDTA (disodium salt). Gold(III) reacts with the reagent to form an orange-yellow chelate[2,3], soluble in chloroform. Interference by gold(III) can be eliminated by reducing the gold with ascorbic acid. Organic masking agents like glycol and mannitol are without adverse effect. Cyanide and pyridine render the test useless and must be destroyed before performing the test.

Detection of palladium in presence of other platinum metals, mercury(I), mercury(II), chromate, permanganate, and ferricyanide ions

One drop of the weakly acidic solution of Pd(II) and other platinum metals is taken into a 5-ml beaker and treated with one drop of the reagent solution and ten drops of water. When the mixture is too acidic, it is neutralized by adding a few drops of 0.5 *M* Na_2CO_3 solution. To the mixture is then added 0.5 to 1 ml of chloroform. The phases are then intimately mixed with an extraction pipet[4] and allowed to separate. The presence of palladium is shown by the yellow color of the chloroform extract.

Detection of palladium in presence of copper(II), iron(II), cobalt(II), nickel(II)

A drop of weakly acidic or neutral test solution is treated in a 5-ml beaker with

10 drops of 0.1 *M* EDTA solution, one drop of the reagent solution and 0.5 to 1 ml of chloroform. The palladium chelate is extracted, separated and observed as described above.

Detection of palladium in presence of gold

A drop of weakly acidic or neutral test solution is treated with one drop of the reagent solution and 10 drops of water and a few drops of 0.5 *M* Na_2CO_3 solution. At the mixture is then added a pinch of ascorbic acid and the mixture is warmed. The gold chelate is reduced to the metallic state. The palladium chelate is then extracted from the mixture and observed as described before.

Sensitivity

In aqueous solution: limit of identification = 1 μg and the dilution limit = 1 : 1,000,000.

In chloroform: limit of identification = 0.5 μg dilution limit = 1 : 1,100,000.

ACKNOWLEDGEMENT

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SUMMARY

A new spot test for palladium is based upon the formation of an orange-yellow chelate with phenyl-α-pyridyl ketoxime. Interference by the metals usually associated with palladium can be easily and completely prevented. Limit of identification: 0.5 μg Pd.

RÉSUMÉ

Une nouvelle réaction à la touche est proposée pour l'identification du palladium. Elle est basée sur la formation du chélate jaune orange, obtenu avec la phényl-α-pyridylcétoxime.

ZUSAMMENFASSUNG

Palladium reagiert mit Phenyl-α-pyridylketoxim unter Bildung eines orangegelb gefärbten Chelates. Diese Reaktion kann als Tüpfelprobe für Palladium verwendet werden.

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SEPARATION OF NIOBIUM AND TANTALUM FROM ZIRCONIUM WITH SALICYLHYDROXAMIC ACID

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The determination of niobium or tantalum in the presence of zirconium is difficult, because zirconium almost always coprecipitates. The potassium carbonate fusion method[1] allows the separation of niobium and zirconium within certain limits, but the separation from tantalum is less satisfactory. Schoeller's[2,3] pyrosulfate–tannin method proved to be inadequate when a small quantity of zirconium was present with a large amount of earth acids. Alimarin and Frid[4] recommended the use of pyrogallol as a sequestering agent to keep titanium and zirconium in solution and thus to separate them from niobium and tantalum. Salicylhydroxamic acid[5-7] proved effective for the estimation of zirconium[8] at a pH between 2.5 and 6.5; the interference of titanium was avoided by complexation with hydrogen peroxide.

Salicylhydroxamic acid has recently been found to be applicable for the separation and determination of zirconium in presence of niobium, which is not precipitated from sulphuric acid–hydrogen peroxide solution at any pH. The separation of zirconium from tantalum is not satisfactory as tantalum always coprecipitates even when double precipitation is used.

EXPERIMENTAL

The chemicals used were all of reagent grade; pH adjustments were made with the aid of indicator papers.

Standard solutions of niobium and tantalum: A weighed quantity (0.1–0.2 g) of niobium or tantalum pentoxide (Specpure, Johnson and Matthey) was fused in a silica crucible with ten times its weight of potassium bisulfate, extracted with a mixture of 140 ml of water, 50 ml of hydrogen peroxide (20 vol) and 10 ml of conc. sulphuric acid and made up to a definite volume. The niobium or tantalum content was determined in an aliquot by the cupferron method[10] after the removal of hydrogen peroxide by boiling.

A weighed quantity of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) was dissolved in water containing a little hydrochloric acid and made up to a definite volume with water. The zirconium content of the solution was determined in an aliquot as the oxide.

Salicylhydroxamic acid, m.p. 168–170°, was prepared by the procedure of Bhaduri[6]. A freshly prepared 1% solution of the reagent in hot water was used as the precipitant.

Procedure

To a solution of niobium and zirconium containing 5% (v/v) sulphuric acid and 5–10% (v/v) of hydrogen peroxide (20 vol) was added an excess of the freshly prepared reagent solution. The pH of the solution was then adjusted to above 2.5 with dilute ammonia. The zirconium precipitate was filtered and washed with a hot solution, containing 1% ammonium nitrate and 0.1% reagent. The precipitate was then ignited and weighed as ZrO_2. For reprecipitation, the ignited oxide was fused with bisulfate, extracted with sulphuric acid–hydrogen peroxide solution, and treated as above. The filtrates and washings were evaporated to about 200 ml. When all the hydrogen peroxide had decomposed, the niobium was determined either by the N-benzoyl-N-phenylhydroxylamine method[9] or by the cupferron method[10]. For the separation from tantalum the same procedure was followed.

The data in Table I indicate that the separation of zirconium from niobium is satisfactory and that the method can be conveniently applied for the analysis of zirconium–niobium alloys. In the presence of tantalum the zirconium values always have a positive error of 1–3 mg. Even redissolution and reprecipitation fail to give correct results.

TABLE I

Taken mg			*Found mg*		
ZrO_2	Nb_2O_5	Ta_2O_5	ZrO_2	Nb_2O_5	Ta_2O_5
36.0[a]	10.8[a]	—	36.0[a]	10.6[a]	—
72.0[b]	10.8[b]	—	72.3[b]	10.6[b]	—
180.0[b]	10.8[b]	—	180.6[b]	10.5[b]	—
36.0[a]	27.0[a]	—	35.7[a]	27.2[a]	—
9.0[b]	108.0[b]	—	9.4[b]	107.9[b]	—
9.0[b]	236.0[b]	—	9.3[b]	235.2[b]	—
12.0[b]	—	12.0[b]	13.4[b]	—	10.8[b]
36.0[b]	—	12.0[b]	38.1[b]	—	9.9[b]
12.0[b]	—	145.8[b]	14.8[b]	—	142.8[b]

[a] single precipitation. [b] double precipitation.

SUMMARY

Salicylhydroxamic acid can be used for the separation of zirconium from niobium above pH 2.5 in presence of hydrogen peroxide. Niobium can be precipitated from the filtrate with N-benzoyl-N-phenylhydroxylamine.

RÉSUMÉ

L'acide salicylhydroxamique est proposé comme réactif pour la séparation du zirconium d'avec le niobium. Ce dernier peut être ensuite précipité dans le filtrat par la N-benzoyl-N-phénylhydroxylamine.

ZUSAMMENFASSUNG

Salicylhydroxamsäure lässt sich zur Trennung des Zirkons von Niob verwenden. In dem Filtrat kann Niob mit N-Benzoyl-N-Phenylhydroxylamin gefällt werden.

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THE QUANTITATIVE ANALYSIS OF MIXTURES OF CORROSIVE HALOGEN GASES BY GAS–LIQUID CHROMATOGRAPHY

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INTRODUCTION

Many processes in the atomic energy industry involve volatile corrosive fluorides and their degradation products. A knowledge of the precise chemical form and the amount of each component present in a process gas stream is necessary for efficient plant control. This requirement has led to studies of non-destructive analytical techniques, with the aim of providing an on-line analyser for corrosive gas mixtures containing halogen fluorides and hydrogen fluoride.

ALLEN AND ELLIS[1] concluded that the method of fractional distillation was inapplicable to the problem, because hydrogen fluoride formed azeotropic mixtures with other halogen compounds, *e.g.* chlorine trifluoride and bromine pentafluoride. HAMER, LEECE AND BENTLEY[2] found that nuclear magnetic resonance spectrometry could not be applied to the problem, because halogen exchanges between components in a mixture caused collapse of spectra. Some success was obtained with corrosive gas mass spectrometry (BENTLEY, HAMER AND EVANS[3]) but is was concluded that the method could not be made adaptable for the rapid handling of large numbers of samples.

The first separations of halogen fluorides by gas–liquid chromatography were reported by ELLIS AND IVESON[4]. Since these separations were achieved, the work has been considerably extended and the potentialities and limitations of the technique have been more precisely defined.

EXPERIMENTAL

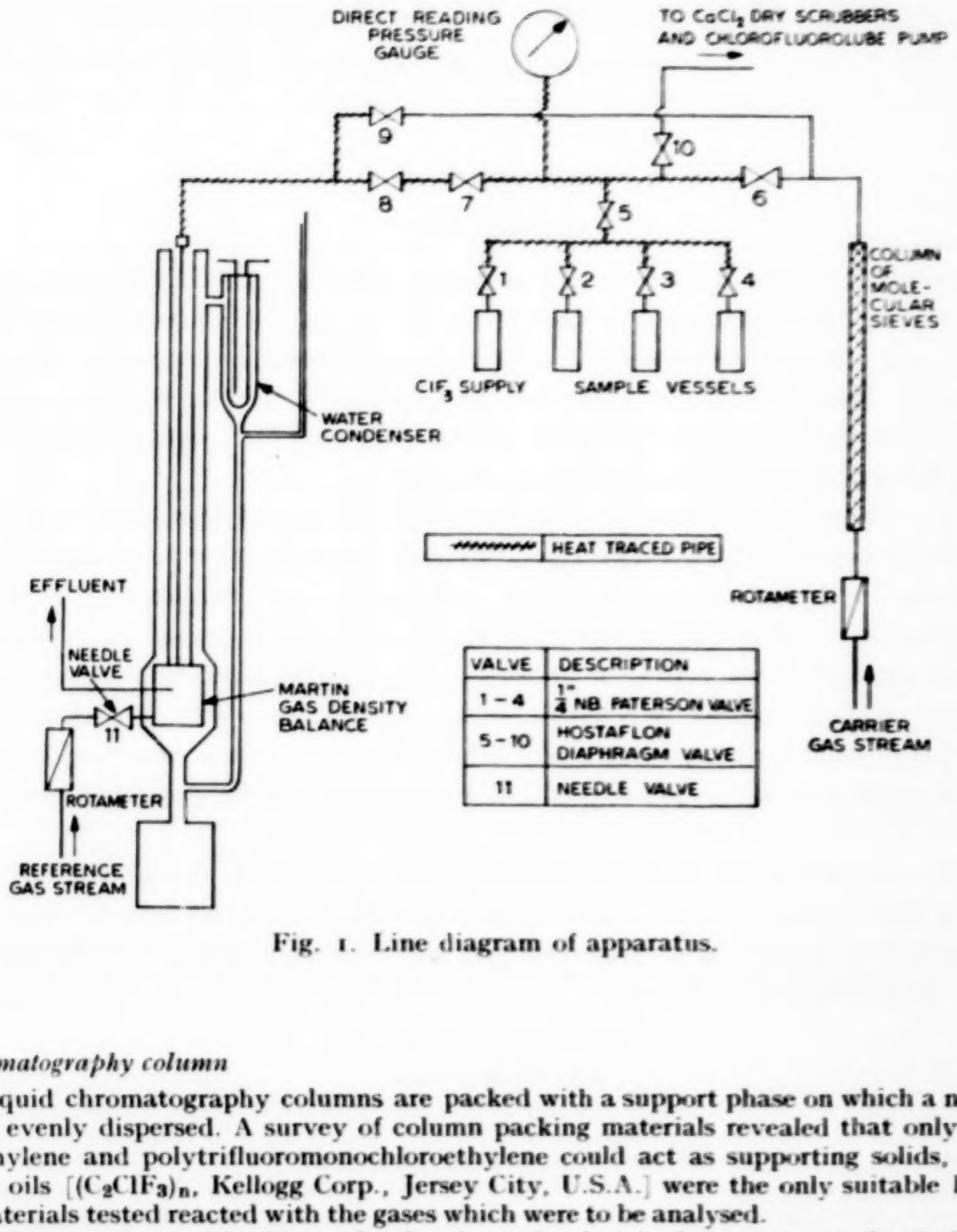
Design of apparatus

Static corrosion tests with chlorine trifluoride and hydrogen fluoride showed that the only suitable major constructional materials for the quantitative handling of corrosive halogen gases up to 60° were nickel, Monel, polytetrafluoroethylene (P.T.F.E., Fluon) and polytrifluoromonochloroethylene (Hostaflon, Kel-F).

A line diagram of the present apparatus is given in Fig. 1. The apparatus is best considered as three parts, *viz.* sample introduction system, column and detector.

Sample introduction system

All pipework in this system was of $\frac{1}{4}$ in. internal diameter nickel tubing, and all joints were either welded or brazed. Two types of valve were used. Paterson $\frac{1}{4}$ in. nominal bore chlorine valves (Paterson Eng. Co., London) were found suitable for the sample bottle manifold. At first, these were internally nickel-plated before use, but subsequent tests showed that no significant errors were introduced by using the standard commercial items with an aluminium-bronze body. For isolation of the sample volume and the remainder of the vacuum system, $\frac{1}{8}$ in. nominal bore diaphragm valves were used. These had bodies and plugs machined from nickel, nickel-plated return springs, and diaphragms made from 1/16 in thick Hostaflon sheet. For pressure measurement a nickel diaphragm pressure transmitter was first employed, but it was found that no significant error was introduced when this was replaced by a direct-reading beryllium–copper capsule pressure gauge (0–1000 mm, Appleby & Ireland Ltd., Basingstoke) piped up to the rest of the equipment with nickel tubing. Heat tracing was extensively used in the sampling system, pipework so traced being held at 50° to enable easy manipulation *in vacuo* of uranium hexafluoride.


DIRECT READING PRESSURE GAUGE
TO $CaCl_2$ DRY SCRUBBERS AND CHLOROFLUOROLUBE PUMP
9
10
8
7
5
6
1
2
3
4
COLUMN OF MOLECULAR SIEVES
ClF_3 SUPPLY
SAMPLE VESSELS
WATER CONDENSER
HEAT TRACED PIPE
EFFLUENT
ROTAMETER
NEEDLE VALVE
MARTIN GAS DENSITY BALANCE
11
ROTAMETER
REFERENCE GAS STREAM
CARRIER GAS STREAM

VALVE	DESCRIPTION
1 – 4	$\frac{1}{4}$" NB PATERSON VALVE
5 – 10	HOSTAFLON DIAPHRAGM VALVE
11	NEEDLE VALVE

Fig. 1. Line diagram of apparatus.

Gas chromatography column

Gas–liquid chromatography columns are packed with a support phase on which a non-volatile liquid is evenly dispersed. A survey of column packing materials revealed that only polytetrafluoroethylene and polytrifluoromonochloroethylene could act as supporting solids, and Kel-F polymer oils [$(C_2ClF_3)_n$, Kellogg Corp., Jersey City, U.S.A.] were the only suitable liquids. All other materials tested reacted with the gases which were to be analysed.

Two columns were used in this work, 4ft. 6 in. and 11ft. 6 in. long, respectively, the latter being in three straight sections. The packing normally used was a 50% w/w loading of Kel-F grade '10' oil on ground Fluon powder sieved to 30–60 B.S. mesh.

Detector

The detector used in this work was a Martin gas density balance (*cf.* MARTIN AND JAMES[5,6]) which has the primary virtue of a sensing element which is never in contact with gas being analysed. It has also been shown[4] that a katharometer made from corrosion-resistant materials can be used for corrosive-gas detection. The density balance was constructed specially for this study by Dr. A. J. P. MARTIN, and differed from the model described in the literature[6] in that the drillings in the block were simulated by a skeleton of welded Monel tubing which was subsequently cast into a block of copper. Current was supplied to the anemometer heater of the density balance by a suitable bridge circuit in which a barreter (Ediswan type B.U. 280/20) operated at 2.8 A but gave a fixed heater current of 1.65 A. The output of the double thermocouple in the anemometer was led directly to a Honeywell-Brown high-speed electronic recorder with two available scales of 0–100 μV and 0–1 mV. The whole of the column and detector assembly was housed in a lagged jacket which was heated with the vapour of 1-chloro-2,2-dichlorotrifluoroethane (b.p. 48°). The need for a dummy column for the reference side of the density balance was eliminated by using a needle valve linked to a short coil of Monel pipe housed within the vapour jacket.

ANALYTICAL PROCEDURE

Carrier gas

In this work argon was normally used as carrier gas. Nitrogen was found to be satisfactory for compounds other than hydrogen fluoride. The small difference in molecular weight between nitrogen and hydrogen fluoride reduced the sensitivity of the density balance to hydrogen fluoride to about half that when argon is used. Helium was not a satisfactory carrier gas, the greater difference in molecular weight between carrier gas and eluted components being much more than offset by the reduced sensitivity of the anemometer, arising from the high thermal conductivity of helium (*cf.* MARTIN AND JAMES[6]).

Before it entered the sampling system the argon was freed from water by passing through a column 5 ft. long and 0.5 in. internal diameter, filled with Linde type 4A molecular sieves which had been activated by heating to 300° *in vacuo* for one hour. Copper pipework was used throughout the argon supply system, and suitably calibrated rotameters were used for flow measurement.

Introduction of sample

A sample of gas is introduced into the sample volume (enclosed by valves 7 and 8 on Fig. 1) from one of the vessels on the supply manifold by suitable vacuum operations. The pressure is recorded, the sample volume isolated and surplus gas is exhausted by the chlorofluorolube-filled scavenge unit which is protected by dry scrubbers containing calcium chloride. Appropriate valve operations then enable the sample to be swept into the column. Free space between the top of the column and the sampling system was packed with dry solid phase to eliminate diffusion effects, following MARTIN[7].

RESULTS

Retention times for two typical columns are given in Table I. A recorder chart speed of 2 in./min was used in compiling elution curves. The pressure drop across column A was 50 mm Hg and 140 mm Hg across column B.

The theoretical plate efficiencies of these two columns A and B to chlorine trifluoride (after KEULEMANS[8]) were approximately 100 and 220, respectively. The feasibility of analysing mixtures of many volatile inorganic fluorides by the gas chromatographic technique is immediately seen. It is also seen that certain fluorocarbon derivatives can be separated from certain corrosive gases.

Typical calibration curves for the response of the detector based on peak height measurements for various amounts of gas are given in Figs. 2 and 3. In general the more linear over-all calibrations are given by non-polar materials. Hydrogen fluoride, which appears as a negative peak (as its molecular weight is less than that of the carrier gas, argon) is the least sensitive to detection and gives the most unsymmetrical elution curves, with pronounced tailing. Peak height sensitivities for components eluted from the longer column are lower because the elution curves are all broader.

TABLE I

Compound	*Retention time (minutes) for elution peak maximum*	
	A *4ft. 6 in. column with argon rate 16.5 cm³/min*	*B* *11ft. 6 in. column with argon rate 27.5 cm³/min*
Nitrogen	1.2	2.0
Chlorine monofluoride	1.4	2.7
Hydrogen fluoride	1.7	3.4
Chlorine	2.0	5.7
Chlorine trifluoride	2.8	8.3
Uranium hexafluoride	10.5	37.5
Bromine	4.55	Not determined
Bromine pentafluoride	6.1	Not determined
Perfluoromethylcyclohexane	11.5	Not determined
Chloroundecafluorocyclohexane	17.0	Not determined

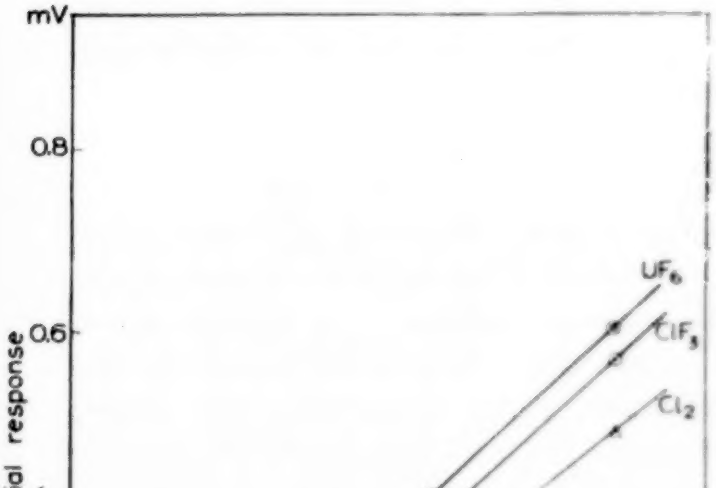


Fig. 2. Calibration curves (4ft. 6 in. column).

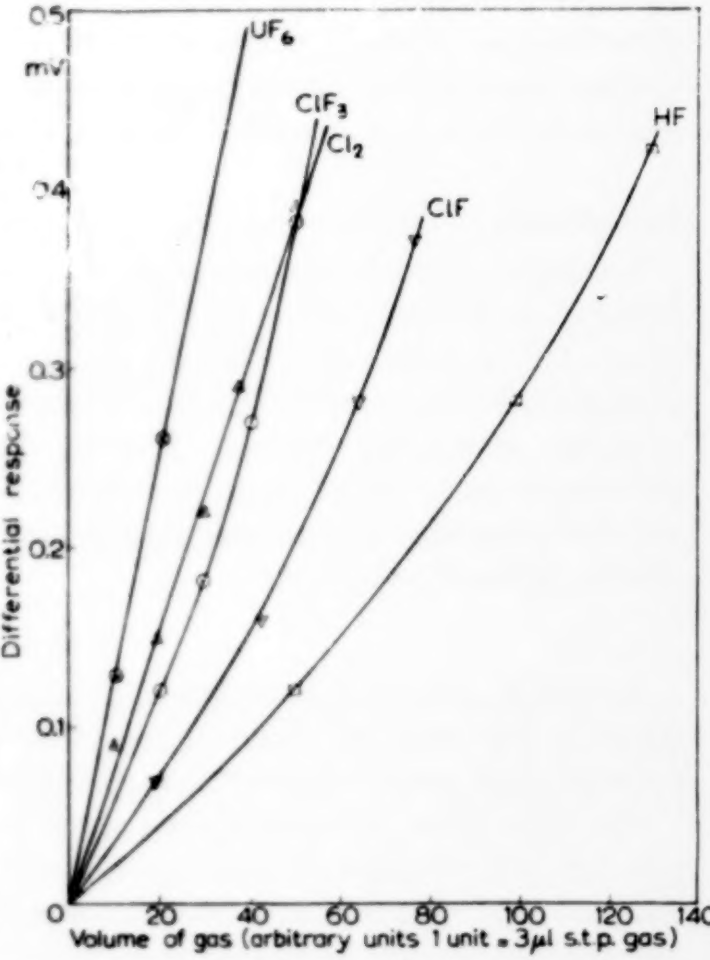


Fig. 3. Calibration curves (11ft. 6 in. column).

Using the 4ft. 6 in. column and the 100-μV scale on the recorder, the minimum reliable level of detection of chlorine trifluoride was found to be approximately 10 μl of s.t.p. gas. This gives rise to a signal of 12 μV measured on elution peak height to an accuracy of about ± 25%. For hydrogen fluoride the minimum reliable detection level was 30 μl of s.t.p. gas, giving a signal of 7 μV peak height to an accuracy of about ± 25%. Three sources contribute to inaccuracies in detection and measurement of these very small quantities of corrosive gases, namely:

a. The minute changes in input potential fed to the recorder,
b. Sluggishness of recorder response,
c. Measurement of low pressures of reactive gases.

For normal analytical work, when 150 μl of s.t.p. gas of chlorine, chlorine monofluoride, chlorine trifluoride or uranium hexafluoride are present in any gas mixture sample, the amount present can be measured to within 1% of the determined value. For hydrogen fluoride, 150-μl samples can be determined within an accuracy limitation of ± 5% of determined value. Accuracies ± 1% with hydrogen fluoride can only be achieved with quantities exceeding 500 μl.

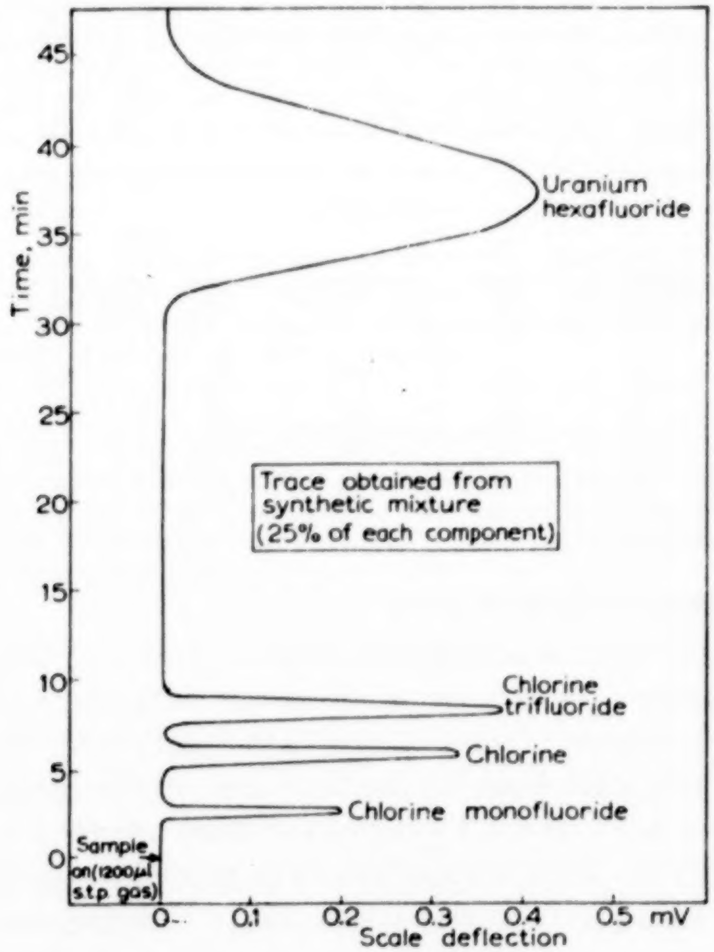


Fig. 4. Specimen trace using 11 ft. 6 in. column.

The validity of results of gas chromatographic analysis of corrosive gases has been extensively checked with synthetic gas mixtures. Some of these analyses using the 4ft. 6 in. column were reported by ELLIS AND IVESON[4]. A typical set of analyses using 1200-μl samples on the 11ft. 6 in. column is given in Table II. A chromatogram from one of these is reproduced in Fig. 4.

The reproducibility of analyses of very small samples of mixtures of corrosive gases is given in Table III. Repeated samples (120 μl of s.t.p. gas) of a synthetic gas mixture were analysed by the standard technique using the 4ft. 6 in. column. The volume composition of the mixture was ClF 5%, HF 57.5%, ClF_3 27.5% and UF_6 10%.

These analyses all fall within the specific limitations of accuracy quoted in previous paragraphs.

TABLE II

REPRODUCIBILITY AND VALIDITY OF ANALYSES OF SYNTHETIC MIXTURES

Sample	Percentage by volume							
	ClF		Cl_2		ClF_3		UF_6	
	Synthetic	Found	Synthetic	Found	Synthetic	Found	Synthetic	Found
1	25	25.0	25	25.2	25	24.9	25	24.9
		25.0		25.0		24.8		25.2
2	10	10.0	30	30.2	40	40.0	20	19.8
		10.0		30.1		40.0		19.9
3	15	15.0	35	34.9	40	40.0	10	10.1
		15.1		34.8		40.2		9.9

TABLE III

REPRODUCIBILITY OF ANALYSES OF VERY SMALL SAMPLES

Sample	ClF		HF		ClF_3		UF_6	
	Signal (μV)	Quantity of s.t.p. gas (μl)	Signal (μV)	Quantity of s.t.p. gas (μl)	Signal (μV)	Quantity of s.t.p. gas (μl)	Signal (μV)	Quantity of s.t.p. gas (μl)
1	7	5	11	60	38	30	9	9
2	10	8	12	66	42	33	12	12
3	7	5	12	66	42	33	9	9
4	8	6	13	72	42	33	12	12

Operation of gas chromatography unit at 24°

Table I shows that the retention times on column A of ClF, HF, Cl_2 and ClF at 48° are quite close together. Tests were made at 24° with the vapour jacket of the column heated with the vapour of monofluorotrichloromethane. There was, however, virtually no change in retention time for the first three of the compounds mentioned. The retention times for ClF_3 and UF_6 increased from 2.8 to 3.1 min and 10.5 to 18.5 min, respectively. Very little is therefore to be gained by lowering the operating temperature from 48° to 24° for the particular mixtures being considered.

DISCUSSION AND CONCLUSIONS

The practical results outlined here show that gas–liquid chromatography is a satisfactory and reliable method for the analysis of highly reactive corrosive volatile halogen compounds. The Martin gas-density balance has been shown to be a suitable detector for work in this field. The principal limitation in the development of the technique for analysis of corrosive inorganic gases lies in the reactivity of the materials being analysed. The only materials which can be used as chromatographic stationary phases and supporting media without reaction with the gases being examined give rise to column packings of very low efficiency, *viz.* 20–30 theoretical plates per foot compared with 3000 theoretical plates per foot obtained by SCOTT[9] for hydrocarbon separations on packed columns.

The technique is potentially applicable to any mixture of volatile inorganic compounds and is being used both for routine analysis of process-gas streams and as a research tool in the laboratory for the investigation of the gaseous products of inorganic chemical reactions.

ACKNOWLEDGEMENT

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SUMMARY

The feasibility of separating many volatile corrosive halogen compounds by gas–liquid chromatography has been demonstrated. The potentialities and limitations of the method when applied to analyses of mixtures containing uranium hexafluoride, chlorine, chlorine monofluoride, chlorine trifluoride and hydrogen fluoride are detailed. The technique appears to be applicable for use generally in process-gas analysis and in the laboratory to research studies on inorganic reactions.

RÉSUMÉ

Les auteurs proposent une méthode par chromatographie gaz–liquide pour l'analyse quantitative de mélanges de composés halogénés volatils et corrosifs. Cette technique pourrait être appliquée à l'analyse de divers mélanges de composés inorganiques volatils et pour l'examen de produits gazeux formés au cours de réactions en chimie minérale.

ZUSAMMENFASSUNG

Es wird gezeigt, dass sich die gas–flüssig Phasenchromatographie zur Trennung vieler flüchtiger, korrosiver Halogenverbindungen verwenden lässt. Die Anwendung zur Analyse von Mischungen, die Halogenfluoride und Fluorwasserstoff enthalten, wird ausführlich beschrieben. Es wird auf weitere Anwendungsmöglichkeiten hingewiesen.

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THERMOLYSIS OF SULPHIDES PRECIPITATED BY SODIUM SULPHIDE

I. SULPHIDES OF ARSENIC, MERCURY, RHENIUM, ANTIMONY AND MOLYBDENUM

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(Received June 8th, 1959)

The use of sodium sulphide as a reagent for precipitating and determining sulphides in gravimetric analysis has been dealt with in a series of papers from this laboratory. Previously, many elements which were precipitated as sulphides had to be weighed in other forms because a homogenous precipitate could not be obtained. The use of sodium sulphide, however, enabled these elements not only to be precipitated as sulphide but also to be weighed in this form. The weights of the sulphides obtained corresponded in most cases to the usual formulae. A systematic study by thermolysis of all the sulphides precipitated by sodium sulphide in gravimetric analysis is desirable in order to obtain fuller information about the behaviour of the precipitates and the correct conditions for weighing.

It has been pointed out[1] that if the sodium sulphide reagent is prepared below 5° there is no appreciable oxidation of the reagent and the precipitates obtained are largely free from sulphur. The thermolysis of such precipitates may therefore give different results from those obtained with sulphides precipitated by other methods. Precipitates which are free from sulphur may be expected to begin to lose weight at a higher temperature than those contaminated with sulphur and this has actually been found in some cases in the present investigation.

EXPERIMENTAL

The reagents used and the methods followed in preparing the precipitates were the same as reported in earlier papers dealing with the estimations of the metals as sulphides. The precipitates taken for thermolysis were in exactly the same condition as the corresponding precipitates just before they are weighed in the estimations of the sulphides.

The thermobalance used was the standard Stanton thermobalance. It was not possible to attain true programme control below 120°. To obtain a linear rate of heating with time automatically the high/low switches were preset, high at 2, low at 1, because the maximum temperature used for the observation was 800°. The rate of heating was $5.3 \pm 0.2°$ per min. As the slope altered abruptly at the change-over point it was necessary to start the cam motor 8–9 min after the furnace was switched on. The thermograms shown in this paper were obtained by plotting different points of the original graph on X and Y axes.

Arsenic pentasulphide. The oven-dried arsenic pentasulphide[2] gave a horizontal level up to 270°. Above this temperature, it began to sublime and at 550° the crucible was empty except for a trace of residue which did not change in weight.

Mercuric sulphide. The oven-dried sample of mercuric sulphide[3] gave a horizontal up to 300°. Dissociation then began from 300–310° and at 500°, the crucible was empty.

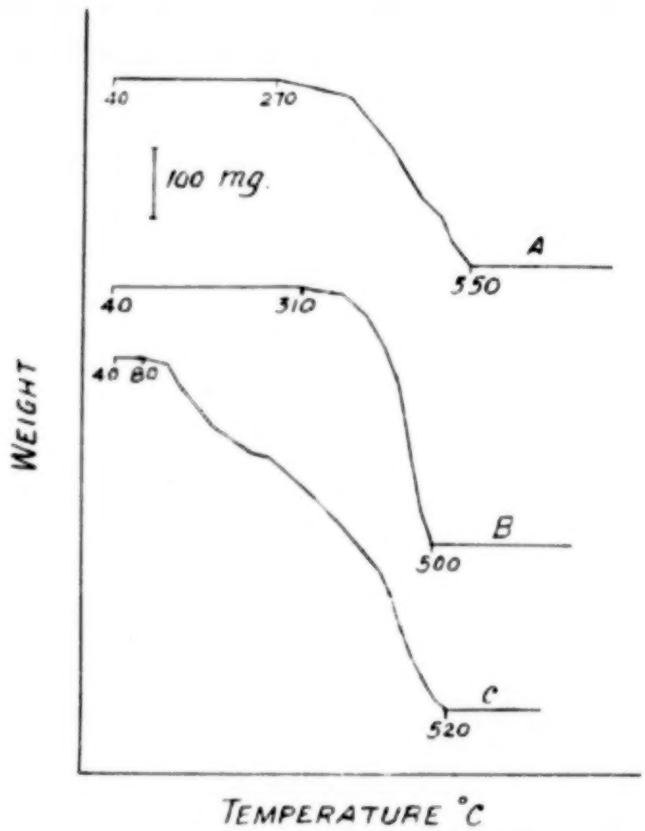

Fig. 1. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent. A. Arsenic pentasulphide, B. Mercuric sulphide, C. Rhenium heptasulphide.

Rhenium heptasulphide. Air-dried rhenium heptasulphide[3] started to lose weight at 80–90° and at 520° the crucible was empty.

Antimony trisulphide. Oven-dried antimony trisulphide[4] gave a horizontal up to 310°. On further heating it oxidized to Sb_2O_3; complete conversion to Sb_2O_3 was indicated by the horizontal at 530–580°. From 580–610° there was a gain in weight corresponding to the conversion of Sb_2O_3 to Sb_2O_4. The horizontal level after 610° corresponded to Sb_2O_4.

Antimony pentasulphide. An oven-dried sample of Sb_2S_5[5] lost weight continuously between 190° and 410°. From 410–570° there was a horizontal corresponding nearly to Sb_2O_4. From 570° there was again a slight loss and the horizontal from 590° onwards corresponded to Sb_2O_4.

Molybdenum trisulphide ($MoS_3 \cdot 2H_2O$). Air-dried molybdenum trisulphide[6] lost 1–2% of its weight at about 80°. There was then a horizontal level up to 170°. From 170°

to 290° the loss in weight corresponded to two molecules of water. From 290–390° the horizontal level corresponded to the anhydrous sulphide. A rapid loss occurred between 390° and 430° after which a horizontal level corresponded to MoO_3 which begins to volatilize at 800°.

In the case of As_2S_5, HgS and Re_2S_7, the precipitate sublimed at a particular temperature while in the case of Sb_2S_3, Sb_2S_5 and $MoS_3 \cdot 2H_2O$ it was converted to another compound which was stable up to 800°. The weights calculated and those actually obtained on heating the last three compounds are given in the following table. The divergence of the actual weights of MoS_3 and MoO_3 from the calculated weights is greater than in the case of antimony.

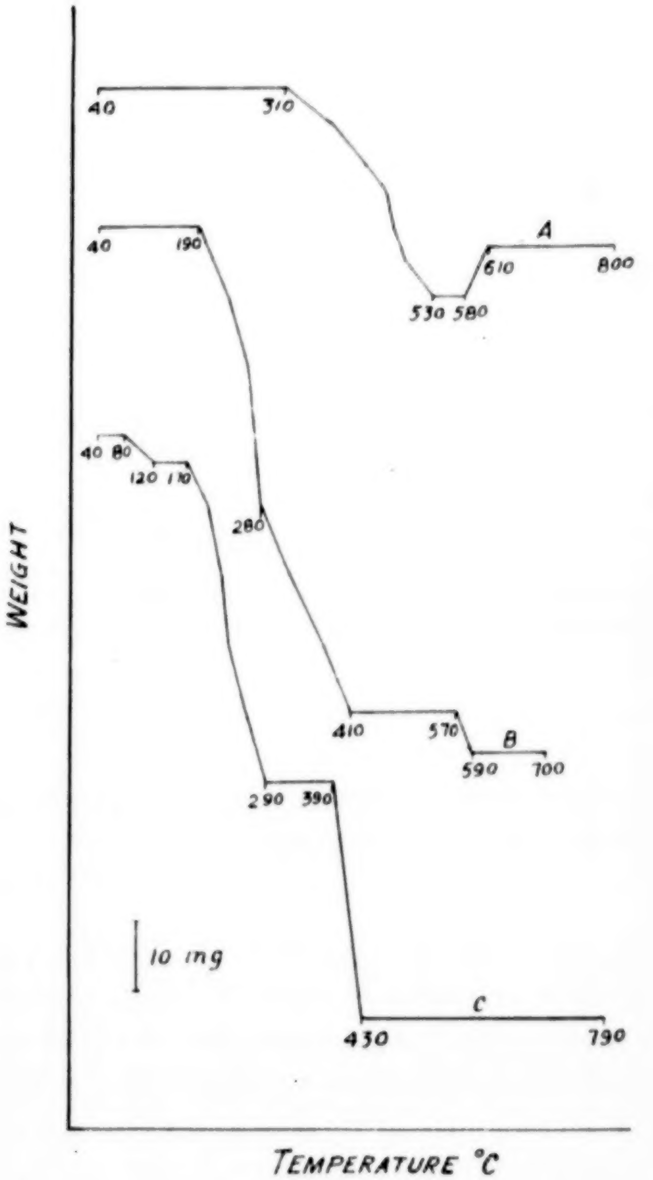

Fig. 2. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent. A. Antimony trisulphide, B. Antimony pentasulphide, C. Molybdenum trisulphide ($MoS_3 \cdot 2H_2O$).

TABLE I

Weight of Sb_2S_3 taken	*Weight of Sb_2O_3 calculated (530–580°)*	*Weight of Sb_2O_3 from graph (530–580°)*	*Weight of Sb_2O_4 calculated (610–800°)*	*Weight of Sb_2O_4 from graph (610–800°)*
258 mg	221 mg	227 mg	233 mg	236 mg
221 mg	190 mg	197 mg	200 mg	202 mg

Weight of Sb_2S_3 taken	*Weight of Sb_2O_4 calculated (590–800°)*	*Weight of Sb_2O_4 from graph (590–800°)*
331 mg	251 mg	256 mg
425 mg	323 mg	324 mg

Weight of $MoS_3 \cdot 2H_2O$ taken	*Weight of MoS_3 calculated (290–390°)*	*Weight of MoS_3 from graph (290–300°)*	*Weight of MoO_3 calculated (430–790°)*	*Weight of MoO_3 from graph (430–790°)*
267 mg	224 mg	217 mg	168 mg	183 mg
266 mg	223 mg	214 mg	168 mg	180 mg

SUMMARY

Thermolysis of the sulphides precipitated by sodium sulphide for direct determination in gravimetric analysis has been studied. It has been shown that the methods used for drying and weighing the precipitated sulphides of arsenic, mercury, rhenium, antimony and molybdenum are reliable.

RÉSUMÉ

Les auteurs ont entrepris une étude de la thermolyse des sulfures précipités par le sulfure de sodium; on a pu ainsi vérifier que les conditions de séchage et de pesée des sulfures d'arsenic, de mercure, de rhénium, d'antimoine et de molybdène convenaient à leur dosage gravimétrique.

ZUSAMMENFASSUNG

Durch Thermolyse der mit Natriumsulfid gefällten Sulfide konnte gezeigt werden, dass die üblichen Methoden der Trocknung und Wägung der Sulfide von Arsen, Quecksilber, Rhenium, Antimon und Molybdän keine Fehlresultate verursachen.

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ELECTROSTATIC METHODS OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

V. A CHROMATOGRAPH HUMIDISER

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(Received June 26th, 1959)

The 'humidiser' or chromatograph conditioner described in this paper was designed for use in conjunction with BLAKE's automatic zone locator as used to underline each conductive spot as the chromatograph travels across the electrodes[1]. Its employment makes it possible to locate and underline spots which are only very slightly conductive or which contain weakly conductive solutes*.

The 'humidiser' can be used in conjunction with either Rectified Radio-frequency (R.Rf.) or Electrostatic Discharge (Es.D.) methods of zone location.

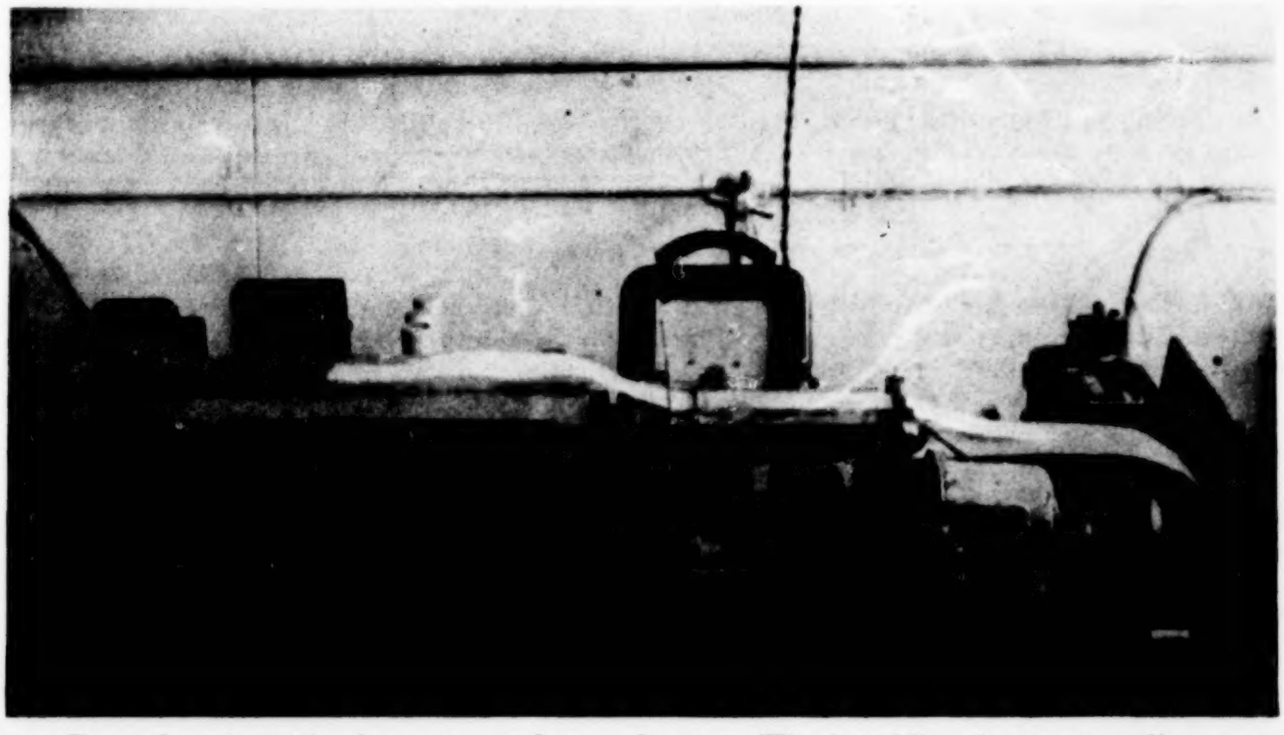

Fig 1. BLAKE's automatic chromatograph zone locator. (The humidiser is seen standing on two wooden blocks to the left of the picture).

Fig. 1 is a photograph of the underlining apparatus[1]. The operational current is supplied from a power pack seen in the background on the left. In the centre there is a relay which controls the magnet (in the centre also). The latter causes a pencil attached to the free end of the magnet's armature to mark the underside of the chromatograph as it is drawn across by means of the small electric motor on the right of the photograph.

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* No staining is required and it is not necessary for the spots to be visible.

This automatic apparatus worked quite reliably in the rather damp laboratory situated in the basement of the old chemistry building, however when it was moved to an air-conditioned laboratory in the new chemistry building the atmosphere was often too dry, and on those occasions it was found necessary to condition the chromatographs by passing them through steam or enclosing them in a humidor immediately before commencing zone location[1,2].

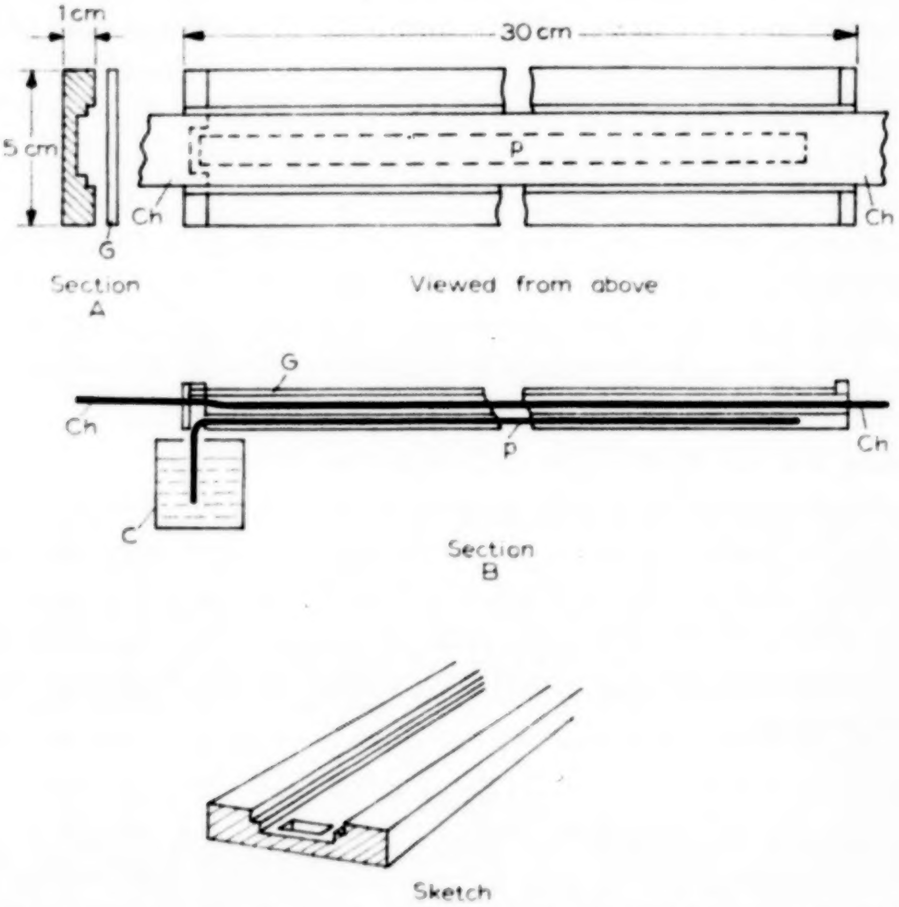

Fig. 2. This is a diagram showing the construction of the "humidiser" made of polystyrene and grooved as indicated. The water container is seen under it on the left.

Realising that a better method was needed the writer devised the "humidiser" described in this paper. This keeps the chromatograph sufficiently moist, and renders automatic zone location reliable under all the varying atmospheric conditions.

The humidiser is attached to the top of the zone locator and as close to the electrodes as possible. It consists of a strip of polystyrene, groved as indicated in Fig. 2. Section 'A'. In the centre of the figure Section 'B' there is a container 'C' filled with water, into which dips the end of a narrow strip of wet filterpaper 'P'. This lies along the bottom of the deepest groove.

The chromatograph 'Ch' rests comfortably across the upper groove and is thus prevented from touching the wet paper below it; above the chromatograph is placed a removable sheet of glass which seals the chamber.

Evaporation from the wet paper is sufficiently rapid to allow the chromatograph to be pulled through the humidiser for zone location only a few seconds after it has been placed therein. The humidiser can be employed also in conjunction with **Blake**'s R.Rf. zone localizer when that instrument is required only for locating the zones, before they are excised and their content is dissolved[3].

While testing the possibilities of using the humidiser for R.Rf. work the following phenomenon was observed.

The spot edge effect

The needle of a 60–0–60 micro-ammeter was set by zero-shunt at 0 for the clean portions of a strip of filter-paper which was spotted with N cobalt chloride. The strip was unconditioned* and the atmospheric humidity at the time was 66%.

When the spot was passed across the electrodes it was noticed that the zero reading for the paper extended right up the edge of the spot, at both front and back edges of the latter, and at that point the meter deflections (at both edges) read 1.5 μA.

The strip was then placed in the humidiser for 2.5 min; this increased the meter reading (on both edges of the spot) to 13 μA. It was observed that the zero position had shifted very slightly towards the negative side of the 0 in the scale of the meter.

After a further 5 min exposure to moisture in the humidiser the zero had shifted back further to —1 μA, and the meter reading for the spot had increased to 37 μA.

After a further 20 min in the humidiser the zero had shifted back to —3 μA, and the meter reading for the spot edges had increased to 90 μA.

From these observations it would appear that the spot being more hygroscopic than the filter-paper absorbed moisture more rapidly. Not only did it obtain water from the atmosphere but it also robbed moisture from the paper in its vicinity, suggesting a steady influx of moisture all round the spot. This phenomenon may provide a satisfactory explanation for the slight irregularity of the base line on solute distribution by current graphs.

SUMMARY

This paper describes a "humidiser" or conditioner employed to sensitise chromatographic spots of weakly conductive solute. It may be used with **Blake**'s R.Rf. or his Es.D. methods. Special reference is made to its use in conjunction with automatic zone location. A photograph of this apparatus is reproduced. 'The spot edge effect' is recorded. (A phenomenon observed during spot localization).

RÉSUMÉ

L'auteur décrit un dispositif ,,humidificateur" permettant de sensibiliser les spots chromatographiques de solutes peu conducteurs. Il peut être utilisé conjointement avec l'appareil automatique de localisation des zones.

ZUSAMMENFASSUNG

Es wird eine als ,,Humidiser" bezeichnete Einrichtung beschrieben, die erlaubt, Flecken von schlecht leitenden Substanzen besser zu lokalisieren. Die Vorrichtung kann in Verbindung mit einem Apparat zur automatischen Festlegung der Zonen verwendet werden.

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* "Unconditioned" implies that the spot had been allowed to dry in the air over night, and was passed through the localizer just as it was.

RÉACTIONS COLORÉES DE STÉROÏDES

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(Reçu le 27 mai 1959)

Les réactions colorées des substances stéroïdiques sont fort nombreuses. Quoique de très légères modifications (fonctionnelles ou spatiales) du noyau stéroïdique puissent influencer sensiblement le comportement réactionnel des composés envisagés, ceux-ci demeurent difficiles à caractériser par des moyens simples et rapides quand il s'agit de produits proches parents. Nous proposons ici quelques réactions colorées de certaines substances qui présentent (dans un squelette relativement important) de faibles modifications structurales.

PARTIE EXPÉRIMENTALE

Réactions sulfuriques

L'action de l'acide sulfurique seul est généralement négligeable, cependant on observe quelques colorations et surtout le développement de fluorescences. Si l'addition d'acide acétique à l'acide sulfurique modifie parfois la réaction, c'est cependant l'addition d'un oxydant qui s'avère surtout favorable.

Les réactions que nous avons décrites antérieurement pour les A^+ ont été reprises pour les stéroïdes et les résultats obtenus ont été consignés dans le Tableau I.

Il ressort de ce tableau que ce sont surtout les dérivés hydroxy-3,Δ_5 qui réagissent avec les divers oxydants. La méthyltestostérone pourtant s'avère positive alors que la testostérone fournit une réaction négative.

Parmi les oxydants, il faut surtout signaler l'acide periodique, le sélénite, le perborate et le persulfate. Une mention spéciale revient au molybdate qui, en présence d'acide acétique, réagit avec de nombreux stéroïdes.

Réactions molybdiques

Si l'on utilise un réactif acétique d'acide molybdique (contenant un peu d'acide sulfurique), on constate qu'on obtient des réactions positives avec un grand nombre d'hormones, de stéroïdes et de façon générale de substances à noyau phénanthrénique. Toutefois la cinétique de la réaction diffère; les dérivés non saturés réagissent plus rapidement et plus facilement. La position d'une ou de plusieurs doubles liaisons (parfois de la fonction OH) paraît fréquemment influencer le développement de la coloration. L'action de la chaleur amenuise les écarts et on obtient dès lors des résultats similaires pour des substances de nature différente. (Tableau II)

L'ergostérol (doubles liaisons) réagit donc aisément. Une mention spéciale revient à l'acide abiétique*. La réaction est fortement positive avec le réactif molybdique.

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* La réaction est fournie par l'acide abiétique mais reste négative avec l'acide déhydroabiétique (éther méthylique). Nous remercions le Prof. Dr. SANDERMANN, du Bundesforschungsanstalt für Forst u. Holzwirtschaft (Reinbek/Hamburg) pour l'envoi de ces 2 échantillons.

TABLEAU I

Stéroïdes	*Ac. sulfurique + ac. acétique*[a] *(a)*	*(b)*	*chlorure de fer(III)*[a]	*sélénite de sodium*	*ac. periodique*	*perborate de sodium*	*sulfate de cerium(IV)*	*persulfate de sodium*	*molybdate de sodium*
cortisone acétate			—	—	—	—	—		bleu
prégnènolone			rouge	rouge					bleu
prednisolone		[c]	trace rouge	—	—	—	—		bleu
prednisone			—	—	—	—	—		bleu
progestérone			—	—	—	—	—		bleu
hydrocortisone acétate			—	—	—	—	—	—	bleu
folliculine			—	brun	—	brun	—	—	bleu
dipronionate de méthylandrostènediol	trace violet	brun	bleu-violet	rouge violet	violet	violet intense	trace violet	violet	bleu
méthylandrostènediol	trace violet	brun	bleu violet	rouge violet	violet	violet intense	trace violet	violet	bleu
désoxycorticostérone acétate	jaune	vert	—	—	—	—	—	—	bleu
monobenzoate d'oestradiol	vert	brun	—	vert	—	—	—	—	—
méthyltestostérone	vert	brun	—	rouge	rouge	rouge	trace rouge	—	bleu
testostérone propionate	—	trace brun	—	—	—	—	—	—	bleu
testostérone			—[b]		—	—	—	—	

(a) = réaction annulaire. (b) = après mélange des solutions.

[a] Colonne 2 et suivantes ont trait à des réactions annulaires.

[b] Après 24 heures, belle coloration verte de tout le mélange et bande spectroscopique.

[c] La prednisolone peut être déterminée en présence de prednisone. Le produit dissous dans l'acide acétique (contenant 15% d'acide sulfurique en volume) développe à chaud (sans addition d'oxydant) une belle coloration violette. La prednisone ne donne pas cette réaction. L'acide sulfurique sans acide acétique conduit au charbonnement.

On obtient également une réaction positive avec les résines renfermant cet acide (colophane, etc.).

TABLEAU II

Substance	*Quantité de substance nécessaire (en µg) pour obtenir D.O. = 1 (10 mm, 650 mµ)*	
	à froid[a]	*après 10 min au bain-marie bouillant*
Strophantine	340	40
Ouabaïne	∞	44
Acide abiétique	54	27
Cholate de sodium	1800	51
Cholestérol [b]	26	21
Ergostérol	30	12

[a] Substance dissoute dans 2 ml d'acide acétique p.a. On ajoute 0.5 ml réactif molybdique (0.5 ml de solution aqueuse de molybdate de sodium à 50% dans 25 ml d'acide acétique) et 0.5 ml d'acide acétique contenant 15% d'acide sulfurique en volume. Après 3 h on ajoute encore 5 ml d'acide acétique.

[b] Nous avons déterminé le cholestérol dans le sérum sanguin par cette méthode (0.01 ml). Les résultats sont cependant parfois plus élevés que ceux obtenus par les méthodes classiques.

Réaction des „corticostéroïdes"

Nous avons finalement traité les divers stéroïdes par une solution acétique de molybdate de sodium, sans acide sulfurique, et constaté qu'on obtient des réactions positives avec la prednisone et la prednisolone. La réaction n'est cependant pas due à la présence de 2 doubles liaisons Δ_{1-4}, puisque la Δ_{1-4} androstadiène, 17β-ol,3-one, fournit une réaction négative.

testostérone	—	desoxycorticostérone acétate	—
testostérone propionate	—	hydrocortisone acétate	—
dipropionate de testostérone	—	cortisone acétate	—
méthyltestostérone	—	prednisolone	+
folliculine	—	prednisone	+
monobenzoate d'oestradiol	—	androstane 3α,17β-diol	—
pregnènolone	—	androstane 3β,17β-diol	—
progestérone	—	androstène diol 3β,17α	—
*trans*déhydro-androstérone	—	androstène 3β,17β-diol	—
*epi*déhydro-androstérone	—	alloprégnane 3β,20α-diol	—
méthylandrostènediol	—	Δ_5-prégnène 3β,20α-diol	—
diproprion. de méthylandrostène diol	—	Δ_{1-4} androstadiène 17β-ol,3-one	—
		acide 3β-hydroxy Δ_5 étiocholénique*	—

Il ressort de ce tableau que ni les 17–OH ni les 3–OH ou =O, ni même les 2 doubles liaisons Δ_{1-4} sont responsables d'une réaction positive. Les réactions négatives que nous avons obtenues au début avec la cortisone et l'hydrocortisone étaient dues au fait que ces dernières se présentent sous leurs formes acétylées. Il est donc possible de déterminer la cortisone ou l'hydrocortisone libre en présence de leurs dérivés éthérifiés. Toutefois la desoxycorticostérone libre fournit également une réaction positive.

Cette réaction n'a cependant rien de commun avec la réaction molybdique de HEARD ET SOBEL[1] ou celle de SCHWARZ[2] puisque ces réactions sont positives avec les dérivés dits γ-cétols ou α,β,3-cétoniques non saturés.

Dans notre cas, seul le groupement „corticostéroïde" réducteur développe la réaction et des substances telles que la progestérone ou la testostérone par exemple (positives dans les réactions de HEARD ET SOBEL ou SCHWARZ) ne réagissent pas*.

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* Nous remercions la firme Roussel-Uclaf pour l'envoi de cet échantillon.

Dosage de la cortisone libre: La cortisone est dissoute dans l'acide acétique. On porte à 3 ml avec de l'acide acétique et l'on ajoute 4 ml de réactif (réactif molybdique: à 0.5 ml de solution aqueuse de molybdate de sodium à 25% on ajoute 40 ml d'acide acétique). Après 2 heures on mesure à 650 mμ.

Prise d'essai (μg)	*D.O. (10 mm)*	*D.O./10 μg*
25	0.077	0.031
50	0.140	0.028
100	0.280	0.028
150	0.450	0.030
200	0.600	0.030
250	0.720	0.029
300	0.890	0.030
100 μg cortisone libre	0.297	
100 μg cortisone libre + 2500 μg acétate de cortisone	0.307	
200 μg cortisone libre	0.565	
200 μg cortisone libre + 2500 μg acétate de cortisone	0.595	
2500 μg acétate de cortisone	0.002	
100 μg hydrocortisone libre	0.207	
100 μg hydrocortisone libre + 2500 μg acétate d'hydrocortisone	0.217	
200 μg hydrocortisone libre	0.425	
200 μg hydrocortisone libre + 2500 μg acétate d'hydrocortisone	0.445	
2500 μg acétate d'hydrocortisone	0.003	

Réaction des Δ_5-stéroïdes

Par addition d'un oxydant à l'acide sulfurique on obtient surtout des réactions positives avec les Δ_5-stéroïdes, tel qu'il ressort du Tableau I. Nous avons tenté d'utiliser d'autres acides. En remplaçant l'acide sulfurique par l'acide perchlorique (70%, $d = 1.67$) nous conjuguons l'action de l'acide à celle de l'oxydant. Les résultats sont cependant peu encourageants. L'addition d'un oxydant s'avère utile. Surtout l'acide iodique et le chlorate de potassium produisent de belles réactions. Toutefois le sélénite de sodium développe la réaction la plus intense. Cette réaction rappelle quelque peu certaines réactions décrites par d'autres auteurs telles que les réactions de PONTIUS[3] pour les stéroïdes à noyau aromatique, et surtout celle de WITTEN ET STONE[4] pour les 3-OH Δ_5-stéroïdes (effectuée sur chromatogramme). Rappelons que le chromatogramme est soumis à l'action du phénol, du molybdate de sodium et de l'acide perchlorique, et porté à une température de 75°.

Dans notre cas, la réaction effectuée en tube à essai peut avoir lieu sans addition de phénol, quoique la présence de phénol soit favorable. Le remplacement du molybdate par le sélénite nous permet d'obtenir une réaction à température ordinaire et de toutes façons quelque soit la réaction effectuée (sur chromatogramme ou par voie humide) le remplacement du molybdate par le sélénite augmente la sensibilité de la réaction. L'*épi*- et la *trans*déhydroandrostérone ainsi que le méthylandrostènediol fournissent des réactions positives. La méthyltestostérone contrairement à la testostérone est également positive.

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* Les réactions du type formazane (rouge ou bleu de tétrazolium), quoique fort différentes, présentent quelque analogie.

Dosage du méthylandrostènediol: On dissout le méthylandrostènediol dans 1 ml de solution alcoolique de phénol à 50%. On ajoute 0.10 ml de réactif (1 g de sélénite de sodium dans 5 ml d'eau), puis 2.5 ml d'acide perchlorique. Après 3 heures on mesure à 610 mμ (Beckmann, 10 mm).

µg	*D.O.*	*D.O./10 µg*
12.5	0.112	0.091
25	0.237	0.094
50	0.475	0.095
100	0.960	0.096
150	1.370	0.092

Dosage de l'épidéhydroandrostérone: On dissout la prise d'essai dans 2 ml de solution phénolique à 50% dans l'alcool. On ajoute 0.40 ml de réactif (1 g de sélénite de sodium dans 5 ml d'eau), puis 5 ml d'acide perchlorique. Après 30 min on mesure à 510 mμ (Bausch et Lomb, tube de 12 mm ø).

µg	*D.O.*	*D.O./10 µg*
10	0.070	0.070
15	0.100	0.066
20	0.140	0.070
40	0.265	0.066
80	0.550	0.068
120	0.810	0.067
160	1.100	0.069

La réaction au brome

L'action d'un oxydant en présence de phénol rappelle la réaction classique de HALPHEN[5] utilisée pour l'identification des acides résineux dans les cires, résines, savons, etc. (présence de colophane, acide abiétique).

Rappelons que la substance est dissoute dans une solution phénolique de tétrachlorure de carbone (phénol 1, CCl_4 4). En présence d'acides résineux la solution acquiert une belle coloration violette.

Cette réaction appliquée aux stéroïdes s'est avérée négative (ou négligeable) pour toute une gamme de stéroïdes.

Nous avons préalablement examiné le comportement de dérivés phénoliques autre que le benzophènol.

phénol	+ +	2,4-dichlorophénol	±
p-chlorophénol	+ +	2,4,5-trichlorophénol	±
m-crésol	+	*α*-naphtol	±
m-aminophénol	—	*β*-naphtol	±
p-bromophénol	+	*p*-nitrophénol	—
o-chlorophénol	+		

Seuls le *p*-chlorophénol (surtout), le *p*-bromophénol et l'*o*-chlorophénol ont fourni des résultats intéressants. Ils ne présentent cependant pas d'avantage marqué par rapport au benzophénol ordinaire.

Seul le méthylandrostènediol développe une belle coloration verte. L'*épi*- et la *trans*déhydroandrostérone demeurent négatifs. La spécificité s'en trouve accrue.

Ici également l'acide abiétique fait exception et fournit une réaction positive. L'acide déhydroabiétique reste négative.

*trans*déhydroandrostérone	—	cortisone acétate	—
*epi*déhydroandrostérone	—	prednisolone	—
méthylandrostènediol	+	prednisone	—
acide abiétique	+	hydrocortisone acétate	—
colophane	+	folliculine	—
ac. déhydroabiétique	—	monobenzoate d'oestradiol	—
androstane $3\beta,17\beta$-diol	—	testostérone propionate	—
androstane $3\alpha,17\beta$-diol	—	testostérone	—
androstène $3\beta,17\beta$-diol	trace	progestérone	trace
androstènediol $3\beta,17\alpha$-diol	trace	désoxycorticostérone acét.	trace
Δ_5-pregnène $3\beta,20\alpha$-diol	trace	méthyltestostérone	trace
alloprégnane $3\beta,20\alpha$-diol	—	cholestérol	trace
épiandrostérone	—	ergostérol	trace

Réaction aldéhydique

Quelques réactions de stéroïdes avec certains aldéhydes ont été décrites; ces réactions sont toutefois peu sensibles. Nous avons utilisé le pipéronal, la vanilline et la *p*-diméthylaminobenzaldéhyde. Leur action est peu marquée. Par contre l'*o*-dialdéhyde phtalique s'est avérée favorable.

folliculine	jaune	alloprégnane $3\beta,20\alpha$-diol	—
épiandrostérone	—	monobenzoate d'oestradiol	—
prednisone	—	testostérone propionate	—
progestérone	—	testostérone	—
hydrocortisone	—	pregnénolone	trace
hydrocortisone acétate	—	méthylandrostènediol	violet
désoxycortisone acétate	—	transdéhydroandrostérone	violet
		épidéhydroandrostérone	violet

On obtient des réactions positives avec les déhydroandrostérones et le méthylandrostènediol (la testostérone est négative)*.

Dosage de la folliculine: On ajoute à la prise d'essai (substance sèche) 0.25 ml de réactif (50 mg d'*o*-dialdéhyde phtalique dans 5 ml d'alcool), ensuite 7 ml d'acide chlorhydrique conc. ($d = 1.19$). On mesure à 360 mμ après 2 à 5 min (spectrophotomètre Bausch et Lomb, tubes de 12 mm ø).

µg	*D.O.*	*D.O./10 µg*
2.5	0.038	0.152
5	0.075	0.150
10	0.150	0.150
20	0.280	0.140
40	0.580	0.145
60	0.850	0.141

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* La pregnénolone est également positive (la coloration violette produite dans l'essai à blanc peut être attenuée par addition d'acide acétique).

Dosage de l'épidéhydroandrostérone: La substance est additionnée de 0.20 ml réactif (200 mg d'*o*-dialdéhyde phtalique dans 5 ml d'alcool) et de 5 ml d'acide chlorhydrique conc. ($d = 1.19$). Après 30 min on ajoute 5 ml d'acide acétique p.a. et on mesure à 535 mμ (spectrophotomètre Bausch et Lomb, tubes de 12 mm ø).

μg	*D.O.*	*D.O./10 μg*
12.5	0.033	0.026
25	0.068	0.027
50	0.132	0.026
100	0.263	0.026
150	0.390	0.026
200	0.530	0.026
250	0.680	0.027

La réaction est 12 fois plus sensible que celle à la *p*-diméthylaminobenzaldéhyde.

Réactions d'hétéropolyacides

Sur chromatogramme: Le chromatogramme est traité par une solution alcoolique d'acide silicotungstique et on examine tel quel ou après action de la chaleur:

à froid, apparaissent	à chaud, se développent
dipropionate de méthylandrostènediol	dihydrocholestérol
transdéhydroandrostérone	stigmastérol
méthylandrostènediol	cholestérol
méthyltestostérone	prednisolone
acide abiétique	folliculine
prégnènolone	
ergostérol	

Ces réactions ont été décrites par divers auteurs.

Anhydride acétique: Après action de l'acide silicotungstique, on vaporise de l'anhydride acétique. On obtient à peu près les mêmes spots colorés. Toutefois la coloration est généralement plus intense et déjà à froid, les produits suivants fournissent une réaction positive:

- dihydrocholestérol
- stigmastérol
- cholestérol
- testostérone
- propionate de testostérone
- folliculine
- progestérone

Incontestablement l'anhydride acétique excerce donc une action favorable. Cette modification oriente la réaction dans une direction nouvelle. D'autres substances pourront être caractérisées et surtout des déterminations quantitatives pourront être effectuées sur des stéroïdes en solution.

En solution: Le stéroïde dissous dans l'anhydride acétique est additionné d'acide silicotungstique. La solution est portée à 100°.

	coloration	*fluorescence*
méthylandrostènediol	verte	+
transdéhydroandrostérone	violet-intense	
épidéhydroandrostérone	violette	
androstènediol $3\beta,17\alpha$	jaunâtre	verte + +
androstènediol $3\beta,17\beta$	jaune foncé	verte + +
androstane $3\alpha,17\beta$-diol	nég.	
Δ_5-pregnène $3\beta,20\alpha$-diol	jaunâtre	jaune
androstane $3\beta,17\beta$-diol	nég.	
folliculine	rouge	rouge
testostérone	verdâtre évoluant vers jaune brun	
cortisone	jaune intense	
progestérone	jaune	

a. Dosage de l'épidéhydroandrostérone

La prise d'essai (résidu sec) est additionnée d'une goutte de réactif (1 g d'acide phosphotungstique dans 1.5 ml d'acide acétique; 1 goutte = ± 0.016 ml = ± 10 mg), puis de 0.25 ml d'anhydride acétique. Après 1 h 3/4 de contact on ajoute 10 ml d'anhydride acétique. On mesure alors immédiatement à 570 mμ (Bausch et Lomb, tube de 12 mm ø).

μg	*D.O.*	*D.O./10 μg*
12.5	0.062	0.050
25	0.125	0.050
50	0.240	0.048
100	0.480	0.048

b. Dosage de la folliculine

La prise d'essai (résidu sec) est additionnée d'une goutte de réactif (1.5 g d'acide phosphotungstique dans 2 ml d'acide acétique; 1 goutte = ± 0.016 ml = ± 12 mg), puis de 0.25 ml d'anhydride acétique. Après 1 h 1/2 de contact, on ajoute 10 ml d'anhydride acétique. On mesure alors immédiatement à 560 mμ (Beckmann, 10 mm).

μg	*D.O.*	*D.O./10 μg**
50	0.162	0.032
100	0.330	0.033
150	0.474	0.031

On constate donc que des corps proches parents tels que le transdéhydroandrostérone ou l'épidéhydroandrostérone d'une part et l'androstanediol et les androstènediols d'autre part se comportent de façon différente. Fréquemment, il semble exister un certain parallèlisme avec la réaction de LIEBERMANN**.

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* Les résultats sont donc moins favorables que pour l'épidéhydroandrostérone. On peut obtenir des erreurs relatives de 4–6%.

** Réaction fortement positive pour la méthyltestostérone, négative avec la testostérone.

DISCUSSION

Si nous avons tenté successivement de remplacer le chlorure de fer(III) par d'autres oxydants, et l'acide sulfurique par l'acide perchlorique, nous avons cependant essayé de circonscrire davantage encore le problème en pourvoyant systématiquement au remplacement d'un des solvants ou d'une des substances réagissantes.

Dans la réaction de **Halphen**, on peut substituer de l'acide chlorhydrique ou bromhydrique au brome. Il est donc vraisemblable que c'est l'acide bromhydrique, produit par action du brome sur le phénol, qui déclanche la réaction. Quant au tétrachlorure de carbone, il s'avère également facultatif. On peut obtenir des réactions positives avec le méthylandrostènediol en dissolvant ce produit dans l'acide tri-, di- ou monochloracétique. Si l'acide acétique seul ne fournit point de réaction, celle-ci peut cependant devenir positive par addition d'un oxydant, un peu de chlorure de fer(III) par exemple (bain-marie, repris par chloroforme, coloration bleue).

On peut se passer du chlorure de fer(III) en ajoutant du chlorure de zinc à la solution acétique (réactions au bain-marie). Le solvant acétique peut lui-même être remplacé par de l'alcool octylique par exemple. Enfin, on peut substituer au chlorure de zinc de l'anhydride phosphorique.

Nous croyons donc pouvoir conclure qu'un grand nombre de réactions de stéroïdes, enserrées dans un réseau étroit de conditions opératoires ne présentent de spécificité que pour autant que ces conditions soient respectées. Nous estimons que ce sont avant tout les liquides lyophobes et l'action d'un oxydant qui contribuent au développement des diverses réactions.

RÉSUMÉ

Diverses réactions colorées peuvent servir à l'identification et au dosage de stéroïdes. L'acide molybdique en solution acétique constitue un réactif d'α-cétols libres. Les Δ_5-stéroïdes peuvent être dosés par un réactif au sélénite. La réaction d'**Halphen** et l'*o*-dialdéhyde phtalique ont servi à l'identification et au dosage de certains stéroïdes. Les hétéropolyacides peuvent servir à des fins qualitatives et quantitatives pour autant que ces hétéropolyacides soient utilisées en présence d'anhydride acétique.

SUMMARY

A number of colour reactions for the identification and determination of steroids are described.

ZUSAMMENFASSUNG

Es werden eine Anzahl Farbreaktionen zum Nachweis und zur Bestimmung von Steroiden beschrieben.

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SPOT TESTS FOR THE IDENTIFICATION OF TITANIUM ALLOYS AND THEIR DIFFERENTIATION FROM ZIRCONIUM AND ITS ALLOYS

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INTRODUCTION

During manufacture of the various titanium alloys every precaution is taken to ensure that they retain their identity. Zirconium bearing materials are manufactured in an entirely independent plant and, at this stage, the probability of mixing these with titanium alloys is almost impossible. There are, however, occasions when users of these materials have sought an additional safeguard against inadvertent mixing during fabrication, and it is then desirable to be able to apply a simple confirmatory spot test which will classify these various alloys.

EXPERIMENTAL

Chemical spot tests on metal surfaces are usually based on a preliminary attack of the metal with a drop of a suitable solvent, such as hydrochloric or nitric acid. Titanium, zirconium and their alloys do not readily respond to acid attack in this way, but it has been shown that fluoboric and hydrofluoric acids are both relatively good solvents for these metals[1]. Unfortunately, the presence of fluoride, excess acid, and the preponderance of parent metal in the resulting solution, precludes a straightforward application of many specific cationic reactions. Modifications to known chemical reactions were therefore investigated, with preference for tests incorporating characteristic colour reactions. No attempt was made to develop tests which would differentiate between alloys containing the same alloying metals in different amounts, and a separate test for the identification of aluminium was not investigated, because alloys containing this metal can be more easily identified by a positive reaction given by other metals that normally accompany aluminium, for example tin in Ti/Al/Sn and vanadium in Ti/Al/V alloys.

In the following experimental tests the surface of the metal under test was freshly abraded with fine emery cloth before applying the solvent acid, which was either fluoboric or hydrofluoric acid.

IDENTIFICATION OF TITANIUM ALLOYS

Under the following headings, reactions of the various titanium alloys were considered and relevant factors in the development of suitable tests are outlined. The tests finally recommended have been subjected to extensive trials and the author is satisfied that they serve adequately to differentiate the alloys in question.

The reactions of a particular alloy are quite distinct from those of titanium or any of the other titanium alloys mentioned.

Titanium–aluminium–tin alloy

Three coloured complexes, resulting from reaction with special reagents, are used as a means of detecting tin. They are the so-called 'molybdenum blue' colour, produced by reduction of molybdates and phosphomolybdates[2–4], the violet colour formed with cacotheline[5] and the magenta coloured reaction product with toluene-3,4-dithiol (dithiol)[6].

These reactions were examined, but it was not possible, by simple modification, to overcome interference by titanium in the 'molybdenum blue' and cacotheline reactions. No characteristic colour was produced on the addition of dithiol solution to a Ti/Al/Sn alloy, following initial attack with fluoboric acid, but a pale red colour was formed with dithiol, characteristic of tin, after nitric acid was added to the drop of fluoboric acid solution. The nitric acid appears to dissolve the tin, which darkens the metal surface when only fluoboric acid is used as solvent. Addition of thioglycollic acid to the dithiol solution produced a more distinct pale red colour and delayed formation of a brown colour which appeared on standing.

Titanium–aluminium–manganese alloy

The most suitable test for detecting manganese depends on the formation of permanganic acid by oxidants, such as potassium periodate or sodium bismuthate, in nitric acid solution. After initial attack of the prepared surface with the recommended solvent, the solution was oxidised with nitric acid and solid sodium bismuthate was added, but under these conditions formation of permanganic acid was transient, due to reduction by nitrous acid. Addition of urea, however, to decompose nitrous acid, stabilised the characteristic colour. If the drop was disturbed after addition of sodium bismuthate, the permanganic acid colour faded; the addition of too much sodium bismuthate produced a similar effect.

Titanium–aluminium–vanadium alloy

Several well-known reactions for the qualitative identification of vanadium were tried, following initial attack of the metal surface, but none was entirely satisfactory. The preliminary tests included reduction of ferric iron in the presence of an indicator[7], reaction with α-benzoinoxime[8] and sodium tungstate[9]. It was observed, however, that when a solution of potassium ferrocyanide was added to the test solution a reddish-brown precipitate was obtained, and this was easily differentiated from coloured precipitates produced with titanium or with other titanium alloys.

Titanium–copper alloy

Application of the well-known sodium diethyldithiocarbamate reaction[10] in ammoniacal solution, following initial attack of the metal with fluoboric acid and nitric acid, was entirely satisfactory for identifying copper in titanium–copper alloy.

Titanium–molybdenum alloy

Molybdenum-bearing alloys are more soluble in hydrofluoric acid than in fluoboric acid, and a mixture of hydrofluoric and nitric acids was used as a solvent in the development of a suitable test. Of the tests applied for detecting molybdenum, that based on the formation of molybdenyl thiocyanate[11] proved most satisfactory. The intensity of the red colour produced depended on the concentration of nitric acid present in the solvent and the duration of the initial acid attack. If the nitric acid concentration was greater than (1 + 1), thiocyanate was decomposed, and if less than (1 + 4), the concentration of acid was not sufficient to dissolve molybdenum in the sample. A compromise was a solvent containing 10 ml hydrofluoric acid (1 + 9) and 6 ml conc. nitric acid ($d = 1.42$). This solvent, which must be stored in a polythene container, was stable for at least 24 h. The ammonium thiocyanate–stannous chloride reagent was also stable for a similar period.

IDENTIFICATION OF ZIRCONIUM IN THE PRESENCE OF TITANIUM AND ITS ALLOYS

Three reagents known to give characteristic reactions with either titanium or zirconium are hydrogen peroxide[12], alizarin red S (sodium alizarin sulphonate)[13] and solochrome cyanine R 200[14]. Fluoride was known to interfere with two of the reactions under specified conditions, but the extent of its interference with solochrome cyanine R 200 was uncertain. Titanium reacts with hydrogen peroxide in acid solution to form yellow pertitanic acid; vanadium and molybdenum also produce yellow colours under similar conditions. Fluoride suppresses these colour formations, particularly that produced by titanium.

After initial attack of titanium and titanium alloys with fluoboric acid, a drop of hydrogen peroxide (20 vol) immediately produced a yellow colour, which persisted for several min, and no colour was obtained when the same test was applied to zirconium, zirconium–tin alloy and Zircaloy 2. The test, therefore, clearly distinguishes titanium and its alloys from zirconium and the zirconium alloys mentioned. Very dilute solutions of hydrogen peroxide in the presence of titanium gave either a very transient yellow colour or no colour at all. Some difficulty was experienced in dissolving Ti–Mo alloy in fluoboric acid (10%) but an addition of 1 ml of hydrofluoric acid (40%) to 10 ml of the fluoboric acid solution was effective.

Solochrome cyanine R 200 is a water soluble dye and yields lakes with some metals. An aqueous solution (0.1%), which is blood-red in colour, first turned orange when applied to zirconium and its alloys, but after about 5 min the red colour was restored. With titanium and titanium alloys the drop of reagent decolourised almost immediately.

Alizarin red S is a well-known water soluble dye used for detecting zirconium and several other metals. The aqueous solution produces a red colour with zirconium salts, and this is stable at relatively high acidities, but the zirconium lake is decolourised by fluorides and silico fluorides. When a drop of the aqueous solution was added, after the initial fluoboric acid attack, no colour was observed at first, but a pale red colour developed gradually on standing in the presence of zirconium and its alloys. If the acid drop was allowed to react with the metal surface for about 2 min, before applying the reagent, a pale red colour was formed immediately. It appears that the reduction in acidity, brought about by solution of the metal, together with the relatively high concentration of zirconium in solution, was sufficient to prevent interference by the amount of fluoride present; the colour was stable for at least 20 min.

During the initial acid attack a black spot appeared on the surface of some of the zirconium–tin alloys tested, and this was probably due to the presence of tin. The pale red colour was not so easily seen, and it was prone to fading. With titanium and its alloys, the colour produced was in striking contrast, being dark-blue or green-blue. Alizarin red S is considered to be the most satisfactory reagent.

METHOD

It is advisable, in applying the following differentiating spot tests, to use control samples of known composition.

Before applying any of the tests, abrade the surface of the specimen with fine emery cloth; the surface of the metal must be bright and clean. Apply the acid solvent and reagents by means of a thin glass rod.

Reference to 'other titanium alloys' refers to the titanium alloys on pages 50–52, and reference to zirconium alloys refers to the zirconium alloys on pages 52–53.

(a) IDENTIFICATION OF TITANIUM ALLOYS

Solvents

Fluoboric acid solution. To 280 ml of hydrofluoric acid (40%) (maintained at 10°) add, in small quantities, 130 g of boric acid. Store in a polythene bottle. Dilute 10 ml of this solution with 10 ml of water before use.

Hydrofluoric acid–nitric acid solution. Dilute 5 ml of hydrofluoric acid (40%) to 50 ml with water. Add 30 ml of nitric acid ($d = 1.42$) and store in a polythene container. This reagent must not be kept for more than a few days.

TIN

Special reagents

Dithiol solution. Dissolve 0.2 g of toluene-3,4-dithiol (dithiol) in 100 ml sodium hydroxide solution (1%) and add a few drops of thioglycollic acid. This solution is unstable and must be freshly prepared.

Nitric acid solution (Approx. 2 N). Dilute 15 ml of nitric acid ($d = 1.42$) to 100 ml with water.

Procedure

Apply a drop of dilute fluoboric acid solution. After 3 min add a drop of nitric acid solution (approx. 2 *N*), then one drop of dithiol solution. A pale red colour develops with Ti–Al–Sn alloy. No colour is formed with titanium and other titanium alloys except Ti–Al–V and Ti–Al–Mn, which produce a brown coloured spot after standing for 3–4 min.

MANGANESE

Special reagents

Nitric acid ($d = 1.42$). Add 0.5–1.0 g of urea to about 10 ml of nitric acid ($d = 1.42$) before use, *i.e.* sufficient urea to provide a layer of undissolved solid.

Procedure

Apply a drop of dilute fluoboric acid solution. After 3 min add one drop of nitric acid ($d = 1.42$). Moisten a very thin glass rod and dip into sodium bismuthate powder so that a little solid adheres to the tip of the rod. Transfer the adhering powder to the test drop but *do not stir*. A pink colour develops in 1–2 min in the presence of manganese. If in doubt, view the spot with a hand lens; any pink colouration will be seen at the boundary of the sodium bismuthate. The sodium bismuthate must be added immediately after the addition of nitric acid. No colour is produced with titanium and other titanium alloys.

VANADIUM

Special reagents

Dilute fluoboric acid solution. Mix 20 ml of fluoboric acid solution (see 'Solvents') with 50 ml of water before use.

Potassium ferrocyanide solution (10%). Dissolve 10 g of potassium ferrocyanide in water and dilute to 100 ml.

Procedure

Apply a drop of dilute fluoboric acid solution. After 3 min add one drop of potassium ferrocyanide solution (10%). A reddish brown precipitate is formed if vanadium is present.

Titanium and other titanium alloys give either a green, yellow-green or yellow-brown precipitate.

COPPER

Special reagents

Dilute fluoboric acid solution. Mix 20 ml of fluoboric acid solution (see 'Solvents') with 50 ml of water before use.

Nitric acid solution (1 + 1).

Sodium diethyldithiocarbamate solution (0.2%). Dissolve 0.2 g of sodium diethyldithiocarbamate and 5 g of ammonium citrate in 60 ml of water. Add 10 ml of ammonia solution ($d = 0.940$) and dilute to 100 ml.

Procedure

Apply one drop of the dilute fluoboric acid solution. After 3 min add one drop of nitric acid solution (1 + 1). After a further 2 min add one drop of sodium diethyldithiocarbamate solution (0.2%). A yellow colour develops in the presence of copper.

With Ti–Al–Sn and Ti–Al–Mn alloys, a light brown colour develops in the spot about 2 min after addition of the sodium diethyldithiocarbamate reagent.

MOLYBDENUM

Special reagents

Ammonium thiocyanate–stannous chloride solution. Dissolve 20 g of ammonium thiocyanate in water and dilute to 50 ml.

Dissolve 20 g of stannous chloride ($SnCl_2 \cdot 2H_2O$) in 50 ml of hydrochloric acid (1 + 1). Mix the two solutions. This reagent must be prepared daily.

Procedure

Apply a drop of hydrofluoric acid–nitric acid solution (see 'Solvents'). After 3 min add one drop of the ammonium thiocyanate–stannous chloride solution. A brilliant red colour is formed in the presence of molybdenum. This colour fades after about 30 sec.

Titanium, Ti–Al–V, Ti–Al–Mn, Ti–Al–Sn and Ti–Cu alloys give a yellow colour

(b) IDENTIFICATION OF ZIRCONIUM IN THE PRESENCE OF TITANIUM AND ITS ALLOYS

Solvent

Fluoboric acid solution. To 280 ml of hydrofluoric acid (40%) (maintained at 10°) add, in small quantities, 130 g of boric acid. Store in a polythene bottle. Dilute 10 ml to 100 ml with water before use.

Special reagents

Alizarin red S solution (0.1%). Dissolve 10 mg of alizarin red S in 10 ml of water.

Procedure

Apply a drop of dilute fluoboric acid solution. After 1–2 min add one drop of alizarin red S solution.

A red colour forms with zirconium and zirconium alloys. Titanium and titanium alloys react with the reagent to give a dark blue or green-blue spot, and a pink edge develops in the drop on long standing.

ACKNOWLEDGEMENT

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SUMMARY

During manufacture every precaution is taken to safeguard against inadvertent mixing of titanium and zirconium alloys. There are, however, occasions when confirmation of identity is desirable. Simple spot tests are described for the rapid differentiation of a range of titanium alloys and for distinguishing these materials from zirconium and its alloys. After a preliminary attack of the abraded metal surface with either fluoboric or hydrofluoric acid, characteristic coloured reaction products are formed with well known reagents, and these tests serve to classify the material.

RÉSUMÉ

Des réactions à la touche sont décrites pour identifier des alliages de titane et pour les distinguer du zirconium et de ses alliages. Le métal à examiner est attaqué superficiellement soit par l'acide fluoborique, soit par l'acide fluorhydrique.

ZUSAMMENFASSUNG

Titanlegierungen lassen sich von Zirkonium und seinen Legierungen durch Tüpfelproben der auf Oberfläche der Legierungen nach Anätzen mit Fluoroborsäure oder Fluorwasserstoffsäure unterscheiden.

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SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF INDIUM IN URANIUM AND THORIUM METALS AND THEIR SALTS

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A method has been developed for the spectrophotometric determination of indium in uranium and thorium metals and their salts in the range 0.1 to 10 p.p.m.

According to SANDELL[1], indium can be separated by oxine–chloroform extraction at pH 3.5, but elements such as gallium, aluminium, cobalt, nickel, thallium, tin, molybdenum, iron, vanadium and bismuth interfere by giving coloured extracts.

A method has been described by MAY AND HOFFMAN[1] in which indium and other metals listed above are first extracted with oxine-chloroform solution at pH 4 in presence of ammonium citrate. After the oxinates have been decomposed, indium, aluminium, gallium, thallium and bismuth are extracted with chloroform from an aqueous citrate–cyanide solution at pH 8.5 in presence of cupferron and dithizone. The metals are then transferred to the aqueous solution by shaking the extracts with 1% nitric acid. Finally, indium is determined in alkaline solution containing potassium cyanide and ammonium cyanide with dithizone–chloroform. It is possible to determine 10 μg of indium in presence of 10 mg of copper, zinc and lead; bismuth, tin and thallium interfere.

The oxine–chloroform method cannot be used to separate indium from uranium and thorium at pH 4; the recovery is not quantitative. Recently, REYNOLDS AND SHALGOSKY[2] tried to recover indium from 1 g of zinc by this separation but they were also unsuccessful.

LUKE AND CAMPBELL[3] determined indium in residues from germanium chloride distillation by extraction with dithizone–chloroform from an alkaline solution containing citrate and cyanide, and developing the colour with oxine–chloroform after the decomposition of dithizonates. However, photometric measurement of indium as oxinate in chloroform at 420 mμ showed that it was not sensitive enough for less than 10 μg in 20 ml of oxine–chloroform solution.

Principle

From an alkaline solution containing ammonium citrate and potassium cyanide indium is extracted along with lead, bismuth, thallium and tin[4] by a solution of dithizone in chloroform. The optimum pH of extraction is 8.3–9.6[1]. Bismuth if present in large amounts can be removed by prior extraction with dithizone-chloroform at pH 3.5–4. Stannic tin is not extracted along with indium[3,4].

Indium along with lead and thallium is then extracted back to 1% nitric acid.

Indium alone is then extracted with dithizone–carbon tetrachloride solution at pH 5 to 6 in presence of sodium thiosulphate to complex lead and bismuth[5]. Thallium is not extracted at this pH. The indium content of the sample is determined by measuring the optical density of the organic phase at 510 mμ.

EXPERIMENTAL

Reagents

Distilled water redistilled in glass apparatus was used for preparing all reagents.

Indium solution. 0.5 g of indium metal (spec. pure) was dissolved in a few ml of nitric acid and diluted with water to give solutions containing 0.1, 1, 10 and 100 μg/ml. The first two solutions were prepared as required from the stock solution.

Ammonium citrate solution 50%. 100 g of ammonium citrate were dissolved in 200 ml of water. Dilute ammonia was then added till the solution was blue to thymol blue indicator and impurities were removed by shaking with 0.02% dithizone in chloroform; dithizone was removed by washing with chloroform.

If ammonium citrate is not available then 432 g of citric acid monohydrate (E. Merck) are dissolved in 100 ml of water and about 500 ml of conc. ammonia ($d = 0.91$) is added slowly to the cold solution till just alkaline to litmus. This is diluted to 1 l and treated as above.

10% Ammonium citrate. 20 ml of 50% ammonium citrate solution were diluted to 100 ml with water.

2N Sodium acetate solution. 27.22 g of crystalline sodium acetate (A.R.) were dissolved in water and made up to 100 ml. It was purified by treating with dithizone as above.

Acetate–Acetic acid buffer (pH 5.5). 18 ml of 2 N sodium acetate solution and 20 ml of 0.2 N acetic acid were mixed and diluted to 200 ml and was then purified by shaking with dithizone carbon tetrachloride until the organic layer was distinctly green. It was then washed with carbon tetrachloride to remove dithizone.

10% Potassium cyanide. 10 g of potassium cyanide (E. Merck) were dissolved in 100 ml of water. The required aliquot was treated with dithizone–chloroform just before use.

1% Nitric acid (v/v). 1 ml of E. Merck G. R. grade nitric acid and 99 ml of water were mixed.

0.02% Dithizone in chloroform 40 mg of dithizone (E. Merck) were dissolved in 200 ml of chloroform and the solution was shaken in a separating funnel with 10 ml of strong ammonia and 100 ml of water. The organic phase was rejected and the aqueous layer was washed with 50 ml of chloroform. The organic layer was again rejected. The aqueous layer was cooled and acidified with hydrochloric acid. The dithizone liberated was then extracted with 75 ml of chloroform and aqueous phase rejected. The chloroform layer was once again washed with 100 ml of water. The organic layer was diluted to 200 ml with chloroform and stored in an amber bottle in a cold place.

0.02% Dithizone in carbon tetrachloride. It was prepared as above using carbon tetrachloride instead of chloroform.

0.002% Dithizone in carbon tetrachloride. A fresh solution was prepared as required by diluting 10 ml of the above solution to 100 ml with carbon tetrachloride.

20% Hydroxylamine hydrochloride. 20 g of hydroxylamine hydrochloride were dissolved in 60 ml of water. A few drops of meta-cresol purple were added and the solution was neutralized with ammonia. An excess of a 4% solution of sodium diethyldithiocarbonate was added and extracted with chloroform until no yellow colour was obtained with copper solution. Hydrochloric acid was then added until the solution turned pink. The solution was then diluted to 100 ml with water.

20% Sodium thiosulphate. It was freshly prepared by dissolving 20 g of sodium thiosulphate (A.R.) in 100 ml water and was purified by shaking with dithizone–carbon tetrachloride solution.

PRELIMINARY EXPERIMENTS

The optimum pH of extraction of indium as dithizonate from an aqueous solution containing sodium thiosulphate (2 ml of 20%) was found to be 5 to 6 and the optimum wavelength 510 mμ in agreement with the data of SANDELL for indium dithizonate in the absence of sodium thiosulphate.

PROCEDURE

Standard curve

Indium standards containing 0.25 to 10 μg were prepared and the standard curve was obtained as described below.

Aliquots of standard solution were transferred to 100-ml separating funnels and diluted to 20 ml with water. 10 ml of 10% ammonium citrate were added and the pH was adjusted with dilute nitric acid to 3.5 to 4 using indicator paper. 5 ml of 0.02% dithizone in chloroform were added and shaken for 1 minute. The extraction was repeated 2–3 times until the organic phase remained distinctly green. The organic phases were discarded and the aqueous layer was washed with chloroform.

To the aqueous phase 2 ml of 10% potassium cyanide and 0.2 ml of the hydroxylamine reagent were added. The pH of the solution was adjusted to about 9 with a few drops of ammonia using universal indicator paper. 5 ml of 0.02% dithizone in chloroform were added and the solution shaken for 2 min. The organic phase was transferred to another 100-ml separating funnel. The extraction was repeated 3–4 times. All the organic extracts were collected together in a 100-ml separating funnel and shaken with 20 ml of distilled water for 30 sec. The aqueous layer was rejected. Two more washings were given to remove excess alkali. 20 ml of 1% nitric acid were added to the organic phase and shaken for 2 min to back-extract indium into the aqueous phase. The organic layer was rejected and the acid was washed with carbon tetrachloride to remove all chloroform.

To the acid solution 13 ml of 2 *N* sodium acetate and 2 ml of 20% sodium thiosulphate were added. The pH of the solution was about 5.5. 10 ml of 0.002% dithizone in carbon tetrachloride were added from a 10-ml pipette and the solutions were shaken for 2 min. The first few ml of the carbon tetrachloride layer were rejected, which also served to wash the stem of the funnel. The remaining organic layer was directly transferred to a 1-cm pyrex cell which had been rinsed with the organic phase. The optical density of the solutions was measured with a Beckman DU Spectrophotometer at 510 mμ against water.

The optical densities of the standards taken directly at pH 5 to 6 using sodium acetate–acetic acid buffer with or without thiosulphate agreed with the optical densities of the standards following the complete procedure.

Beer's law was obeyed from 0.25 to 10 μg of indium (Table I).

TABLE I

THE OPTICAL DENSITIES OF STANDARD SOLUTIONS OF INDIUM

With 10 ml of 0.002% dithizone–carbon tetrachloride at 510 mμ

Indium taken μg	*Optical density*	
	I	*II*
0.25	0.015	0.015
0.50	0.028	0.030
1.00	0.055	0.060
2.00	0.120	0.120
3.00	0.190	0.183
4.00	0.235	0.240
5.00	0.300	0.310
10.00	0.615	0.610

Recoveries of indium added to uranium and thorium

Uranium and thorium nitrate equivalent to nearly 5 g of uranyl oxide or thorium oxide was dissolved in the minimum amount of nitric acid and taken to a syrupy state on a water bath. Samples of uranium oxide were treated similarly. Thorium oxide was dissolved in the minimum amount of nitric acid by adding a few drops of 1% hydrofluoric acid to aid the dissolution. Hydrofluoric acid was removed by repeated evaporation with nitric acid.

In the case of uranium and thorium metals, the metal was rinsed with ether and then with water; it was then dried and dissolved in a few ml of nitric acid and taken to a syrupy state on a water bath. 0.25 to 10.0 μg of standard indium were added to the uranyl nitrate or thorium nitrate solutions. The total volume was made up to 20 ml and indium determined as described above.

TABLE II

RECOVERIES OF INDIUM ADDED TO URANYL NITRATE

No.	*Amounts of sample taken (U_3O_8) in g*	*Indium*		*Remarks*
		μg added	*μg recovered*	
1	1.000	Nil	Nil	No indium was indicated
2	1.000	0.25	0.25	
3	1.000	0.50	0.50	
4	1.000	1.00	0.93, 0.97	
5	1.000	2.00	2.00	
6	1.000	3.00	2.92	
7	1.000	5.00	5.00	
8	1.000	10.00	10.00	
9	1.000	5.00	5.00, 5.00*	
10 a	5.000	Nil	Nil**	
10 b	5.000	5.00	5.08**	
11 a	5.000	Nil	Nil***	
11 b	5.000	5.00	4.92***	

No. 9: The following impurities (in μg) were added to one of the samples: Lead 10; Zinc 10; Iron 10; Copper 20; Cobalt 20; Silver 10; Gold 25; Nickel 20; Bismuth 10; Chromium 10.

No. 10 a and b**: The sample contained the following impurities in p.p.m.: Boron 0.2 ± 0.02; Cadmium < 0.05; Nickel < 1; Cobalt < 1; Copper < 1; Iron = 5.5; $As_2O_3 < 1$; Beryllium < 1; Manganese < 1; Chromium < 5; Tin < 1; Zinc < 20; Cerium = 11.5; Gadolanium = 1.5; Dysprosium = 0.58; Erbium = 1.

No. 11 a and b***: The sample contained the following impurities in p.p.m.: Boron 0.35; $As_2O_3 < 1$; Beryllium < 1; Tin < 1; Iron = 9; Cadmium < 0.05; Nickel < 1; Cobalt < 1; Copper < 1; Zinc < 20; Cerium = 0.92; Dysprosium < 0.1; Erbium < 0.1.

When a 5-g sample was taken, 20 ml of 50% ammonium citrate were added instead of 10 ml. Tables II and III show the recoveries of indium added to uranium and thorium. In some of the experiments ions likely to give dithizonates were added to the uranium and thorium salts. These added impurities when taken through the whole process did not show any indium while added indium was recovered as shown in Expts. 9–11 of Table II and Expt. 8 of Table III.

TABLE III

RECOVERIES OF INDIUM ADDED TO THORIUM NITRATE

No.	*Amounts of sample taken (ThO_2) in g*	*Indium*		*Remarks*
		μg added	*μg recovered*	
1	1.000	—	—	No indium was indicated
2	1.000	0.25	0.25	
3	1.000	0.50	0.50	
4	1.000	1.00	0.93	
5	1.000	2.00	0.200	
6	1.000	3.00	3.00	
7	1.000	5.00	5.00	
8a*	5.000	Nil	Nil	No indium was indicated
8b*	5.000	5.00	4.92	

No. 8 a and b*: The following impurities (in μg) were added: Lead 10; Zinc 10; Iron 10; Copper 20; Cobalt 20; Silver 10; Gold 25; Nickel 20; Bismuth 10; Chromium 10.

SUMMARY

A method based on dithizone extraction and determination of indium in the range of 0.1 to 10 p.p.m. in reactor grade uranium and thorium samples is described. Sodium thiosulphate is used as a complexing agent for removing interference by lead and bismuth.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage de microquantités d'indium dans des échantillons d'uranium et de thorium. Elle est basée sur une extraction à la dithizone.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Mikromengen von Indium in Uran- und Thorium Proben. Sie beruht auf einer Extraktion mit Dithizon.

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DETERMINATION OF LOW SULFUR CONCENTRATIONS IN OILS AND ORGANIC SOLIDS

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INTRODUCTION

The petroleum industry has long recognized sulfur as one of the most troublesome contaminants in petroleum streams. It deactivates some catalysts and usually imparts an offensive odor to products; thus, it is important to know and control the sulfur concentration in feeds and product. Recently, the need arose for knowing sulfur concentrations below 200 p.p.m. in waxes and heavy gas oils. Traditional high temperature combustion methods are inadequate at this concentration because of the relatively insensitive titrimetric finishing techniques employed. Lamp sulfur procedures which are normally employed in this range are not applicable to these types of samples; thus, it became necessary to develop a new method.

The first method investigated was based on combustion-nephelometry and involved precipitation of sulfur as barium sulfate. However, poor precision was experienced with this technique. A survey of the literature revealed a colorimetric method by WEST AND GAEKE[1] for measuring sulfur dioxide in air. This method was adapted to a combustion procedure by removing sulfur dioxide from the combustion products by scrubbing through a solution of sodium tetrachloromercurate.

The method is based on the oxidation of sulfur to sulfur dioxide by combustion in a two-furnace apparatus. The evolved sulfur dioxide forms stable, non-volatile disulfitomercurate(II) ion. A red-violet color develops when disulfitomercurate, *p*-rosaniline, hydrochloric acid, and formaldehyde are mixed. The absorption of the solution is measured at 560 mμ and is directly proportional to sulfur concentration.

Sample combustion was carried out in two furnaces at two different temperatures (Fig. 1). Although the analysis can be done with a single furnace, the two-stage method

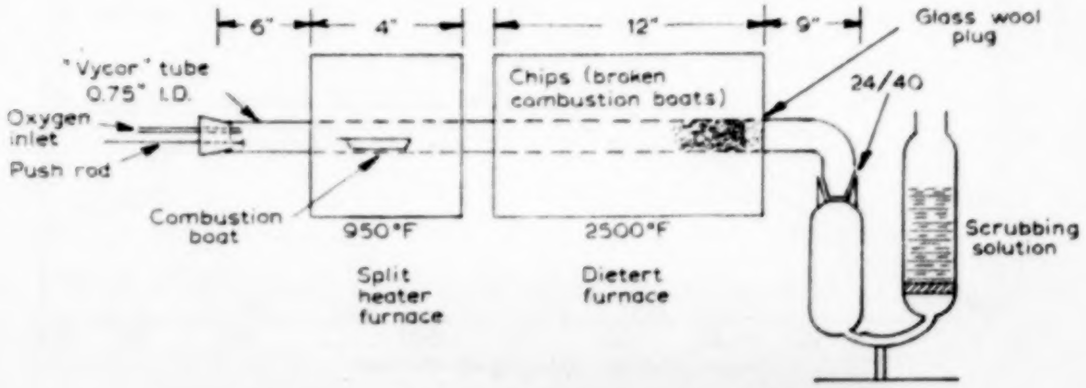

Fig. 1. Two-furnace combustion apparatus.

offers several advantages[2], the most important being improved control of the pyrolysis of the sample. This feature is particularly useful when samples varying in volatility are analyzed.

This procedure has been applied to pure organic solids, waxes, gas oils and residua. As described herein, the procedure is applicable in the range 10–300 p.p.m. sulfur. By reducing the volume of solutions, increasing amount of sample, and/or using wider absorption cells, the minimum level can be lowered substantially. The upper level can be raised by conventional dilution techniques.

EXPERIMENTAL

It is known that when sulfur is burned, an equilibrium $SO_2 \rightleftarrows SO_3$ is set up[3]. This equilibrium is temperature dependent, increasing temperature increasing the percentage of SO_2 present. It is necessary that the temperature used must be such that the percentage of SO_2 formed is independent of small temperature fluctuations in the furnace temperature. By burning known weights of sulfur (as dibenzothiophene) calibration curves at different furnace temperatures were obtained. The results are shown in Fig. 2. This indicates that a temperature of at least 2500°F is desirable. An even higher temperature would be an advantage, but the service factor on the furnaces decreases significantly at higher temperatures. Precision results are shown in Table I.

Results were obtained over a period of several days. This indicated that there was no appreciable day-to-day variation of results.

Blank

A blank is obtained by burning an empty boat in the normal manner, scrubbing and analyzing the combustion products. The main components of the blank are (a)

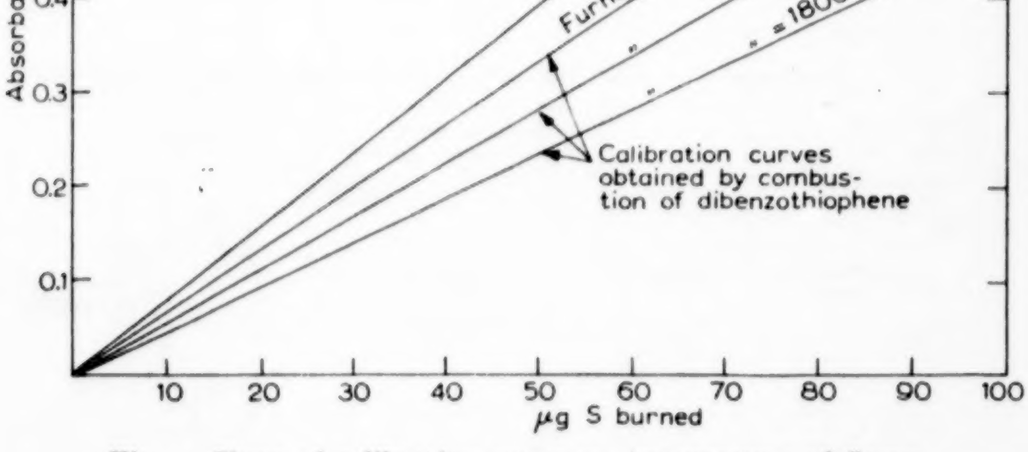

Fig. 2. Slope of calibration curve *vs.* temperature of flame.

TABLE I

PRECISION RESULTS

Sulfur added µg	*Sulfur determined* µg
10	9, 8, 12.5, 10, 12.5, 13, 11, 13 12, 5 Precision: $2\sigma = 3.7$
20	17, 18, 23
30	31, 35
40	37
50	50, 48
70	65, 66
80	78
90	86, 85, 87, 90, 91.5, 93, 92, 90 Precision: $2\sigma = 5.9$
100	101, 104

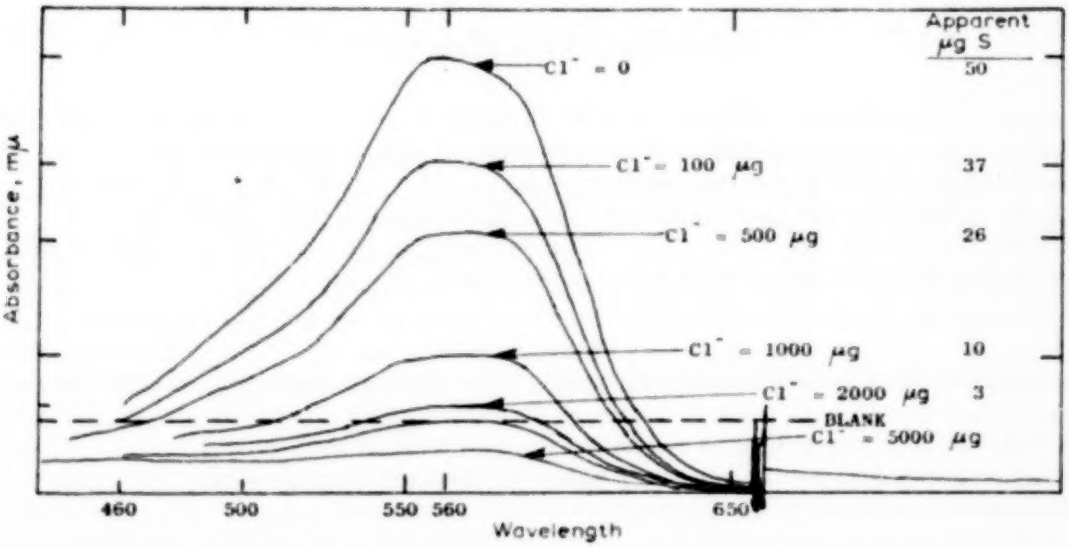

Fig. 3. Interference due to chloride. All samples contain 50 g of S plus various amounts of added chloride. Absorbancy trace obtained on a Cary spectrophotometer.

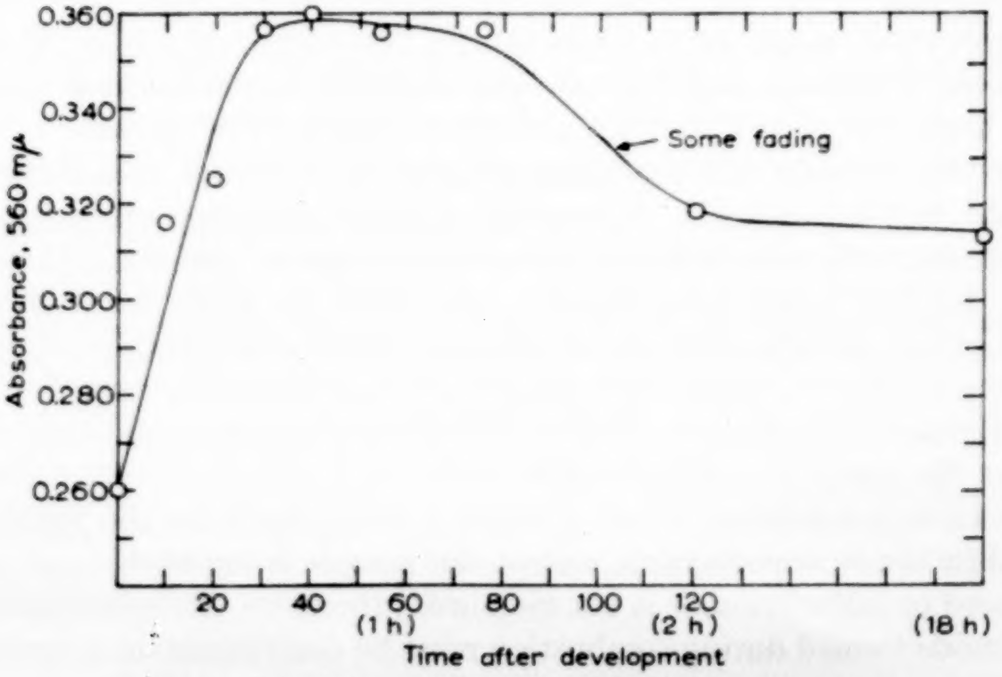

Fig. 4. Stability of color.

sulfur in the oxygen stream, (b) sulfur in the boats, and (c) the color developed from the reagents alone. Results indicate that (a) sulfur in the oxygen stream was negligible, (b) the boats should be burned off at 2500°F and kept in a vacuum desiccator prior to use, and (c) the reagent blank was considerable, but constant for a set of reagents.

Interferences

The effect of the presence of nitrogen or chloride in the sample was determined. This was done by adding known amounts of pure compounds to sulfur samples at the 50 p.p.m. S level. The results as shown by Figs. 3 and 4 indicated that chloride interfered at all levels and nitrogen interfered if present in quantities greater than 100 μg, *i.e.*, 0.01% on a 1-g sample. Both elements bleached the color and seemed to act as oxidizing agents. Experiment showed that inorganic chloride (HCl) and organic chloride (CCl_4) gave similar results.

RECOMMENDED PROCEDURE

Reagents

Sodium tetrachloromercurate solution, 0.1 *M*: Dissolve 20.2 g of reagent grade mercuric(II) chloride and 11.7 g of reagent grade sodium chloride in water and dilute to 1 l.

Hydrochloric acid–bleached para-rosaniline, 0.04%: Mix 40 m of a 1% aqueous solution of *para*-rosaniline hydrochloride and 60 ml of conc. hydrochloric acid; dilute to 1 l.

Formaldehyde, 0.2%: Dilute 5 ml of 40% formaldehyde to 1 l with distilled water.

Sodium bisulfite, reagent grade and *oxygen* (cylinder).

Apparatus

Beckman Model B Spectrophotometer, 1-cm cells (Other suitable spectrophotometers are available).

Furnace, tube type, 4 inch length capable of operation at 1000°F.

Furnace, tube type, 12 inches length capable of operation at 2500°F.

Combustion tube, 0.75 inch ID × 31 inches length, Zirconia.

Assemble the combustion apparatus as shown in Fig. 1. Regulate 4-inch furnace to 950°F and 12-inch furnace to 2500°F. Adjust oxygen rate to 3 l per min. Pour 50–60 ml of sodium tetrachloromercurate solution in scrubber. Depending upon sulfur concentration, weigh up to 1 g of sample into combustion boat. Position boat in center of 950°F furnace and leave it there until the initial burning subsides (2–5 min). Push boat into 2500°F furnace and let it remain there 15 min.

Quantitatively transfer the scrubbing solution to a 100-ml volumetric flask. To the flask add 10.0 ml of acidic *p*-rosaniline solution and 10.0 ml of formaldehyde solution. Fill to mark with sodium tetrachloromercurate solution. Allow to stand 20–30 min for full color development. The color is stable for 1 h. Determine absorbancy of the sample solution at 560 mμ. Read concentration of sulfur from calibration curve (Fig. 2), which has been previously prepared by using fresh standard solutions of sodium bisulfite in sodium tetrachloromercurate solution. The curve should cover the range 0–100 mμ sulfur.

A combination combustion–reagent blank is determined by the same procedure as described in the first paragraph, except the sample is omitted.

Sulfur oxidized to sulfur trioxide is not measured; therefore, the equilibrium amounts of sulfur trioxide formed during combustion must be determined on a pure compound and the necessary correction applied in the calculations. Alternatively, the calibration curve can be determined by burning various size samples of a pure organic sulfur compound. The resulting values will not include the sulfur trioxide formed and a correction factor will not be necessary.

CONCLUSIONS

The method is rapid (30 min per analysis when a group is analyzed), accurate, and precise. Accuracy and precision data obtained on a synthetic sample of 4,4′-thio*bis*-(6-*tert.*-butyl-*m*-cresol) in alcohol are given in Table I. The short term standard deviation is 5.9 p.p.m. sulfur at the 90 p.p.m. sulfur level, and 3.6 p.p.m. S at the 10 p.p.m. level. Chloride interferes at all levels; nitrogen interferes if present in quantities greater than 0.01% for a 1-g sample.

ACKNOWLEDGEMENT

The authors wish to thank C. R. TESSIER who carried out much of the experimental work, and Esso Standard Oil Company for permission to publish this work.

SUMMARY

A rapid and reasonably precise method was needed for determining low sulfur concentrations (< 200 p.p.m.) in organic solids, gas oils, and heavier liquids. This level of sulfur is below the useful range of conventional procedures; therefore, the development of a new method became necessary and a satisfactory combustion–colorimetric method was developed. The method is based on the oxidation of sulfur to sulfur dioxide by combustion and the subsequent formation of stable, non-volatile disulfitomercurate(II) ion. A red-violet color develops when disulfitomercurate, *p*-rosaniline, hydrochloric acid, and formaldehyde are mixed. The absorption of the solution is measured at 560 mμ and is directly proportional to sulfur concentration.

The method is rapid, accurate and precise. The short-term 2-sigma precision limits are 5.9 p.p.m. sulfur at the 90 p.p.m. level and 3.6 p.p.m. at the 10 p.p.m. level. Two samples can be analyzed per hour. The succes of the method is due in part to the use of two furnaces at different temperatures during the combustion step. This arrangement affords good control of the combustion and is particularly useful where various types of samples are to be analyzed.

RÉSUMÉ

Une méthode rapide et précise est proposée pour le dosage du soufre en très faibles concentrations dans des huiles et des substances organiques solides. Elle est basée sur l'oxydation du soufre en anhydride sulfureux par combustion et sur la formation de disulfitomercurate stable non volatil; ce dernier réagit avec la *p*-rosaniline, l'acide chlorhydrique et le formaldéhyde pour donner une coloration violette. L'absorption de cette solution est mesurée à 560 mμ; elle est directement proportionnelle à la teneur en soufre.

ZUSAMMENFASSUNG

Es wird eine rasche und genaue Methode beschrieben zur Bestimmung sehr kleiner Mengen von Schwefel (< 200 p.p.m.) in organischen Substanzen, Gasölen etc. Die Methode beruht auf der Oxydation des Schwefels zu Schwefeldioxyd und Überführung in das stabile, nicht-flüchtige Disulfitomercurat Ion, das mit *p*-Rosanilin, Salzsäure und Formaldehyd gemischt eine rotviolette Färbung ergibt. Die bei 560 mμ gemessene Absorption ist direkt proportional dem Schwefelgehalt.

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SUR LES RÉACTIONS DES IONS DU PLUTONIUM AVEC L'ACIDE ÉTHYLÈNEDIAMINOTÉTRACÉTIQUE

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Le plutonium et le trilon B (sel disodique de l'acide éthylènediaminotétracétique) forment un complexe non ionique, soluble, permettant d'éliminer le plutonium (ainsi que Am et Pb) de l'organisme vivant, où il se trouve probablement, sous forme de plutonium (IV)[1,2]. D'après MILLNER ET WOODHEAD[3], on peut déterminer les ions Pu^{+3} par titrage avec une solution de trilon B (pH = 2,5).

Les complexes du trilon B avec Pu(VI), comme ceux de U(VI)[4,5] et avec Pu(V), comme ceux des ions Me^{+}[6,7], peuvent être utilisés pour la séparation du plutonium d'avec plusieurs éléments, dont les complexes sont plus stables, ainsi que pour la séparation de Pu(IV), Pu(V) et Pu(VI).

PARTIE EXPÉRIMENTALE

Nous avons opéré en solutions perchloriques, les ions ClO_4^- ne formant pas de complexes avec le plutonium[8].

Reactifs

Solutions de $PuO_2(ClO_4)_2$, préparées par oxydations répétées de $Pu(NO_3)_4$ ou $PuCl_4$ (contenant moins de 0.1% de matières étrangères) par l'acide perchlorique à 72%, à l'ébullition; on évapore à sec pour chasser l'excès d'acide perchlorique, et on reprend le résidu par une solution $HClO_4$ 0.5 M + $NaClO_4$ 0.5 M ou par une solution $NaClO_4$ 1.0 M. On vérifie que l'oxydation soit complète par spectre d'absorption. La concentration en plutonium est déterminée en comptant le nombre des particules α ($\pm$1-2%).

Solution de trilon B 0.01 M (recristallisée plusieurs fois) standardisée à l'aide d'une solution de nitrate de plomb 0.01002 M.[9]

Appareillage

La densité optique a été mesurée au spectrophotomètre Beckman DU avec des cuves de 10.0 mm (mesures reproductibles à 0.001-0.005). Les courbes des titrages conductimétriques ont été faites à l'aide du pont de Wheatstone, à température constante (25 ± 0.1)° et fréquence 1000 Hz. Le pH des solutions a été mesuré au potentiomètre LP - 4 à électrode de verre.

1. *Pu(VI) en milieu acide*

Le spectre d'absorption des solutions de $PuO_2(ClO_4)_2$ (0.002-0.017 M) + $HClO_4$ 0.5 M + $NaClO_4$ 0.5 M est identique à celui obtenu en présence de trilon B 0.01 M.

Ainsi, dans les solutions, où $\mu = 1$ et $[H^+] = 0.5\ M$, Pu(VI) ne forme pas de complexes avec EDTA, ou bien, si ces complexes existent, ils sont très peu stables.

2. *Pu(VI) à pH* = 3-5

(a) Solutions avec $\mu = 1$

Après addition d'un fort excès de trilon B à nos solutions, nous avons observé un changement de coloration; en quelques minutes, la solution incolore ou faiblement rose devient jaune citron, et, quelques minutes après elle redevient incolore; au bout de quelques jours, elle reprend une coloration jaune orange, stable. La vitesse des changements de coloration dépend de la quantité de trilon ajoutée.

Tous ces changements ont été suivis par mesures spectrophotométriques; d'après l'abaissement de la densité optique à $\lambda = 835$ mμ, on a pu calculer la diminution de la concentration de PuO_2^{+2} (Fig. 1).

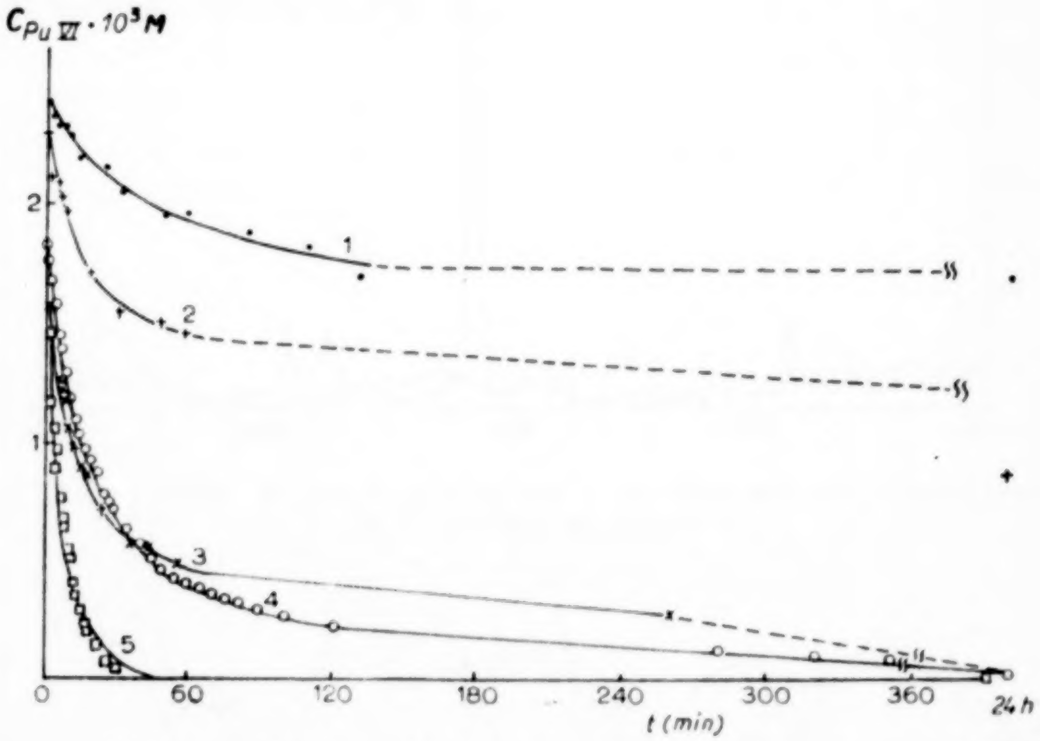


Fig. 1. Changements de concentration de PuO_2^{+2} en présence de trilon B. Solution initiale: $PuO_2(ClO_4)_2$ 0.0029 *M* + $NaClO_4$ 1 *M*, pH = 5; trilon B: courbe 1 = 0.000218 *M*; courbe 2 = 0.000334 *M*; courbe 3 = 0.000435 *M*; courbe 4 = 0.000724 *M*; courbe 5 = 0.00101 *M*.

Il est évident, que: 1) la vitesse de diminution de $[PuO_2^{+2}]$ dépend de la concentration en trilon B; 2) si cette concentration est assez élevée, tous les ions PuO_2^{+2} passent dans un état nouveau, dont l'absorption est différente de celle des solutions de $PuO_2(ClO_4)_2$; 3) dans le cas d'une faible concentration en trilon B, il se produit un équilibre entre les ions ordinaires PuO_2^{+2} et un état nouveau du plutonium; cet équilibre s'établit en 24–48 h.

Les spectres d'absorption des solutions obtenues sont identiques pour toutes les concentrations de trilon B, à condition qu'elles soient assez élevées. On peut voir dans la Fig. 2 un de ces spectres; il diffère fortement du spectre d'absorption de la solution initiale de $PuO_2(ClO_4)_2$ (courbe 1, Fig. 3) et il est tout à fait identique au spectre de la solution obtenue par réduction de PuO_2^{+2} avec l'hydroxylamine (courbe 2, Fig. 3). On sait que celle-ci, dans les conditions citées, réduit quantitativement Pu(VI) en Pu(V)[10].

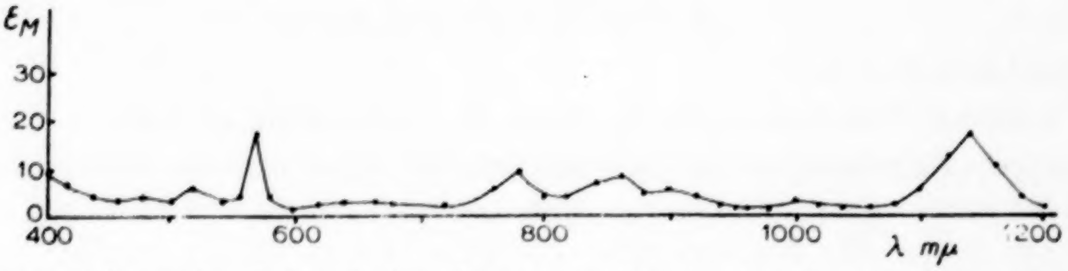


Fig. 2. Spectre d'absorption de la solution obtenue par l'action du trilon sur $PuO_2(ClO_4)_2$ en 24 h.

$$\frac{\text{Concn. trilon B}}{\text{Concn. Pu}} = 0.25$$

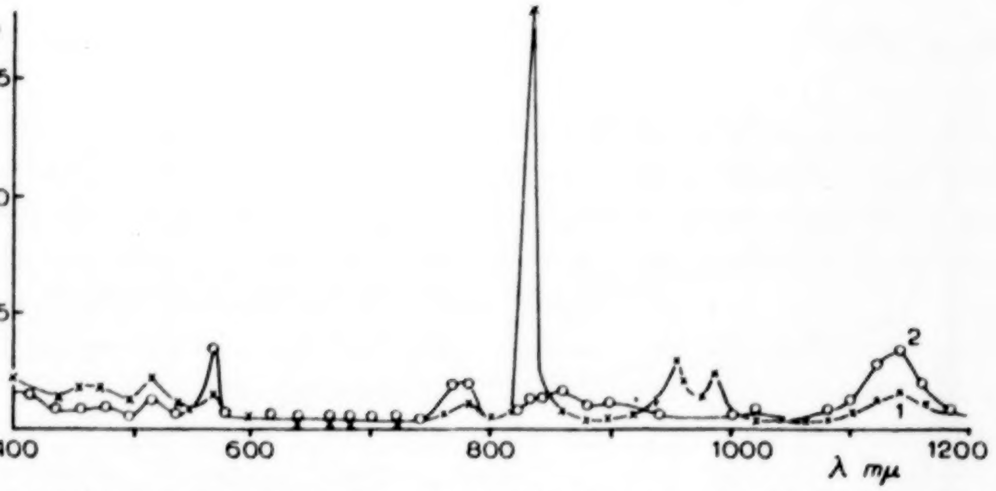


Fig. 3. Spectres d'absorption des solutions: 1. $PuO_2(ClO_4)_2$ 0.0029 *M*, $NaClO_4$ 1.0 *M*. 2. PuO_2ClO_4 0.0029 *M*, $NaClO_4$ 1.0 *M*.

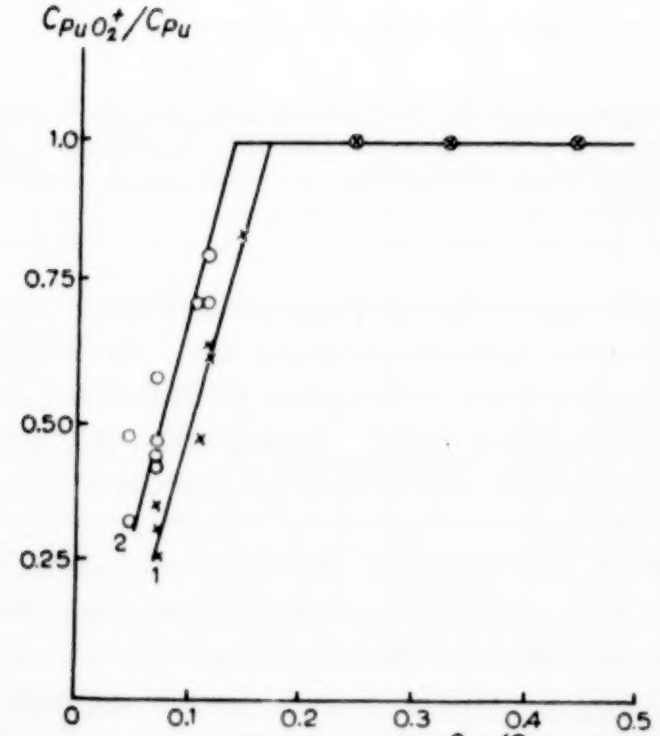


Fig. 4. Degré de réduction de Pu(VI) à (concn. trilon B: concn. Pu) divers. Solution initiale $NaClO_4$ 1 *M*, $PuO_2(ClO_4)_2$ $2.9 \cdot 10^{-3}$ *M*. courbe 1, $[PuO_2^{+2}]$, $\lambda = 955$ mμ. courbe 2, $\lambda = 835$ mμ.

On peut en conclure que le trilon B, en solution $NaClO_4$ *M*, (pH = 3–5), réduit Pu(VI) en Pu(V); la réaction s'effectue en proportions stoechiométriques.

La Fig. 4 nous montre que, pour une réduction complète de PuO_2^{+2} en PuO_2^{+}, il est nécessaire, que la concentration molaire du trilon B soit égale à 0.17 par rapport à la concentration molaire du plutonium, mesurée à λ = 955 mμ; et 0.14 à λ = 835 mμ soit en moyenne: 0.155. Par conséquent, une molécule de trilon B réduit six atomes de plutonium(VI).

Le second changement de coloration, incolore à jaune orange peut être accéléré en chauffant. Le spectre d'absorption de la solution ainsi obtenu est représenté par la courbe 1, Fig. 5. En la comparant avec celle de Pu(V) (Fig. 2), on constate que le plutonium a passé à un nouvel état. La courbe 1 (Fig. 5) représente un spectre d'absorption du complexe Pu(IV)–trilon B, (ressemblance avec spectre de Pu(IV) en présence du trilon B) (courbe 2, Fig. 5).

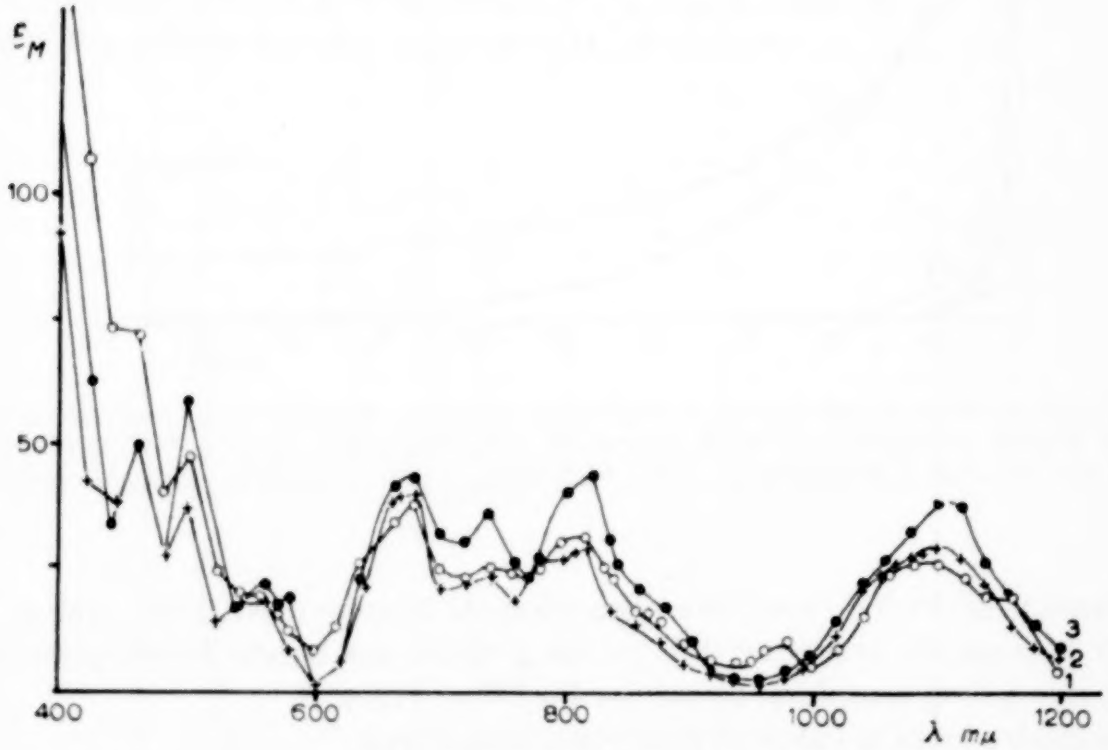


Fig. 5. Spectres d'absorption: 1. Solution Pu(VI) 0.0026 *M* + trilon B 0.0035 *M* + $NaClO_4$ 1 *M*, chauffée 4 h à 80–90° et refroidie; pH = 5. 2. $Pu(NO_3)_4$ 0.0117 *M* + trilon B 0.0148 *M*; pH = 1.35. 3. Pu(VI) 0.0080 *M* + trilon B 0.10 *M*, un mois après préparation; pH = 5.

L'apparition de Pu(IV) est confirmée aussi par la formation d'un précipité de $Pu(OH)_4$, dans le cas où le trilon B est ajouté en quantités insuffisantes (moins qu'équimolaires) pour former le complexe, soluble à pH 3–5.

Il faut remarquer que la réaction de PuO_2^{+2} avec le trilon B est toujours accompagnée d'un abaissement de pH.

(*b*) *Solutions aqueuses sans électrolyte étranger*

En mesurant le changement d'absorption à λ = 835 mμ, nous avons pu déterminer la vitesse de réduction de Pu(VI) par le trilon B dans la solution aqueuse de $PuO_2(ClO_4)_2$ sans $NaClO_4$ (Fig. 6).

Pour faire une comparaison, nous avons tracé la courbe 1 obtenue dans la solution de $NaClO_4$ 1 *M*.

Dans la solution de trilon B 0.1 *M* et de Pu(VI) 0.008 *M* la réduction de Pu(VI) en Pu(V) s'effectue instantanément, on peut observer un accroissement visible de la concentration de Pu(IV) avec une apparition de la coloration jaune orange. Pour observer le cours du processus (Fig. 7), on a choisi une bande d'absorption à λ = 500 mμ, due à l'ion complexe, formé par Pu(IV) et trilon B.

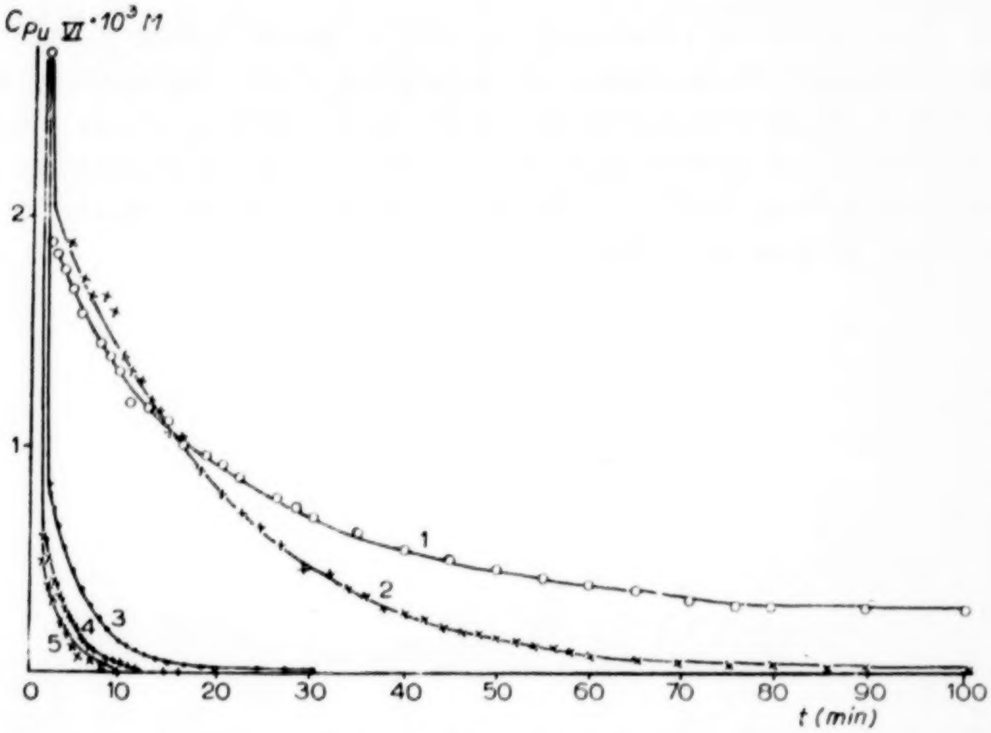


Fig. 6. Changement de concentration de Pu(VI) en présence de trilon B, en fonction du temps. Courbe 1, Pu(VI) 0.0029 *M* + trilon B 0.00072 *M* + $NaClO_4$ 1 *M*. Courbe 2, Pu(VI) 0.0033 *M* + trilon B 0.00094 *M*. Les courbes 3, 4 et 5 Pu(VI) 0.0033 *M* + trilon B 0.0035 *M*; pH = 4.

Après quatre jours la valeur d'absorption change peu.

En absence de $NaClO_4$, on a constaté la même augmentation d'acidité des solutions pendant la réaction entre PuO_2^{+2} et trilon B.

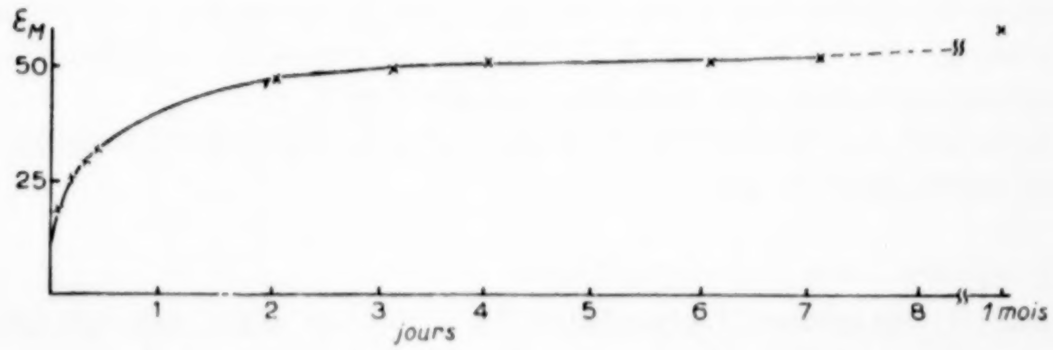


Fig. 7. Changement de coefficient molaire de l'absorption en fonction du temps pour une solution contenant Pu(V) 0.0080 *M* + trilon B 0.10 *M*; pH = 5; λ = 500 mμ.

3. *Réaction entre Pu(V) et trilon B*

On a étudié la formation du complexe Pu(V)-trilon B dans les solutions de PuO_2ClO_4, obtenues par réduction de $PuO_2(ClO_4)_2$ avec l'hydroxylamine.

Différentes quantités de trilon B ont été ajoutées à la solution contenant PuO_2ClO_4 + $NaClO_4$ 1 *M*. En mesurant ensuite pendant deux ou trois heures la densité optique des solutions à $\lambda = 1140$ mμ, 570 mμ et 400 mμ.
On a constaté qu'elle ne variait pas.

Au cours de ces mesures, les solutions sont restées incolores; devenant cependant jaune orange en trois jours, après leur préparation.

L'addition d'un grand excès de trilon B($C_{tr} : C_{Pu} = 0.6 \div 4.7$) à la solution ne change pas, pendant deux heures, le degré d'absorption de la lumière par ce dernier.

Les ions incolores[6,11] forment avec le trilon B des complexes incolores. Ainsi, le comportement de Pu(V), dans la solution contenant le trilon B, a été étudié par titrage conductimétrique. Lors de la première série d'essais, on a titré la solution aqueuse de $PuO_2(ClO_4)_2$ 0.0080 *M*, de pH 3–4.5, par le trilon B.

Dans la Fig. 8 sont représentés les résultats obtenus.

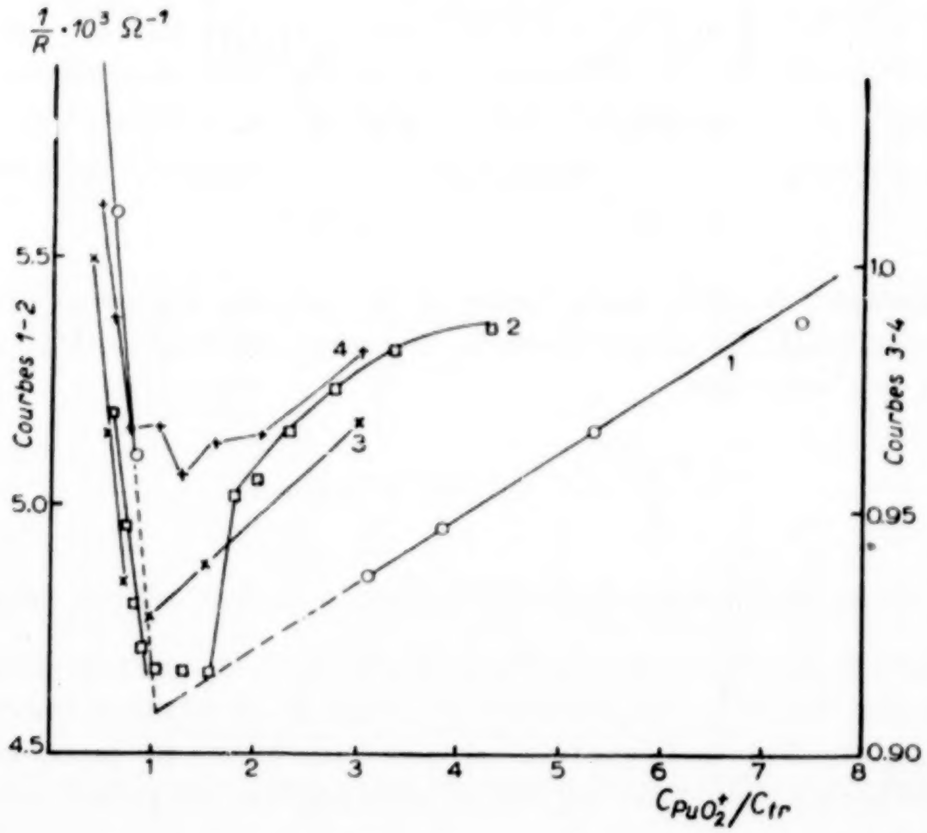


Fig. 8. Titrage conductimétrique de la solution aqueuse de $PuO_2(ClO_4)_2$ par le trilon B. Courbe 1, PuO_2^{+2} 0.0080 *M* et trilon B 0.060 *M*. Courbe 2, PuO_2^{+2} 0.0081 *M* et trilon B 0.162 *M*. Les courbes 3 et 4, PuO_2^+ 0.00066 *M* et trilon B 0.0435 *M*.

Le titrage est d'une durée telle (60 à 100 min), qu'au moment d'arriver à la solution équimolaire du plutonium et du trilon B pratiquement tout le plutonium est à l'état de Pu(V). Les courbes montrent que la conductibilité électrique est minimum dans la région de formation de la solution équimolaire.

On a pu obtenir des résultats plus exacts par titrage conductimétrique rapide, au moyen de trilon B, de la solution PuO_2ClO_4 0.00066 *M* (pH étant 2.4), obtenue par réduction de la solution $PuO_2(ClO_4)_2$ avec l'hydroxylamine.

Avant, ainsi que vers la fin du titrage conductimétrique, la solution de plutonium(V) a été analysée spectrophotométriquement, pour vérifier l'absence du plutonium à d'autres valences.

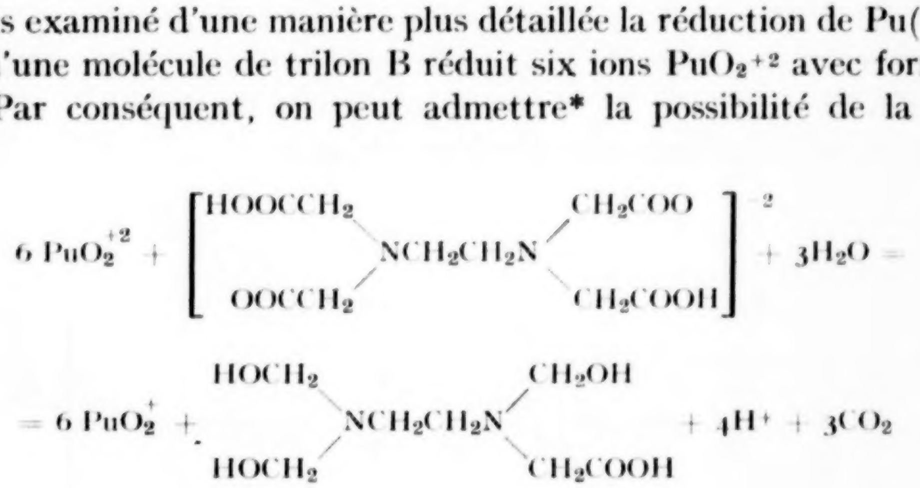
Les courbes 3 et 4 (Fig. 8) confirment que, dans ce cas, dès que le mélange équimolaire PuO_2^+ et trilon B est obtenu, la conductibilité électrique devient également minimum.

Les résultats du titrage conductimétrique indiquent que la formation du complexe trilon B–PuO_2^+ s'effectue dans le rapport 1:1.

DISCUSSION

Nous avons examiné d'une manière plus détaillée la réduction de Pu(VI) en Pu(V).

On sait qu'une molécule de trilon B réduit six ions PuO_2^{+2} avec formation d'ions hydrogène. Par conséquent, on peut admettre* la possibilité de la réaction suivante**.



$$6\,PuO_2^{+2} + \left[\begin{matrix} HOOCCH_2 & & CH_2COO \\ & NCH_2CH_2N & \\ OOCCH_2 & & CH_2COOH \end{matrix}\right]^{-2} + 3H_2O =$$

$$= 6\,PuO_2^{+} + \begin{matrix} HOCH_2 & & CH_2OH \\ & NCH_2CH_2N & \\ HOCH_2 & & CH_2COOH \end{matrix} + 4H^+ + 3CO_2 \qquad (1)$$

Nous avons essayé de déterminer l'ordre de la réaction. On peut supposer que la vitesse de la réaction(I) est proportionnelle à la concentration de PuO_2^{+2} ainsi qu'à celle du trilon B, c'est-à-dire:

$$-\frac{d[PuO_2^{+2}]}{dt} = K\,[PuO_2^{+2}]_t \cdot [\text{trilon B}]_t \qquad (2)$$

où $\frac{d[PuO_2^{+2}]}{dt}$ est le changement de la concentration de PuO_2^{+2} par unité du temps; K = la constante de la vitesse de réaction; $[PuO_2^{+2}]_t$ = la concentration en PuO_2^{+2} au temps t; $[\text{trilon B}]_t$ = la concentration en trilon B au même moment.

On peut conclure d'après l'équation (2) que dans le cas où la concentration du trilon B est suffisante pour nous permettre d'en négliger de petites variations l'expression devient:

$$-\frac{d[PuO_2^{+2}]}{dt} = K_1\,[PuO_2^{+2}]_t \qquad (3)$$

où

$$K_1 = K\,[\text{trilon B}]_{t=0} \qquad (4)$$

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* Nous exprimons notre reconnaissance à A. A. NEMODRUK pour ses conseils à ce sujet.

** Au moment de la présentation de ce travail pour la publication, un article[13] a été publié consacré à l'investigation polarographique des produits d'oxydation de l'EDTA. Les essais de l'auteur apparemment ne sont pas en contradiction avec notre version du mécanisme de la réaction.

Les données expérimentales sur le changement de la vitesse de réaction en fonction de la concentration en PuO_2^{+2} dans des solutions, renfermant du trilon B (en quantité six fois celle nécessaire à la réduction complète du plutonium (VI)), sont représentées par les courbes 1–3 (Fig. 9).

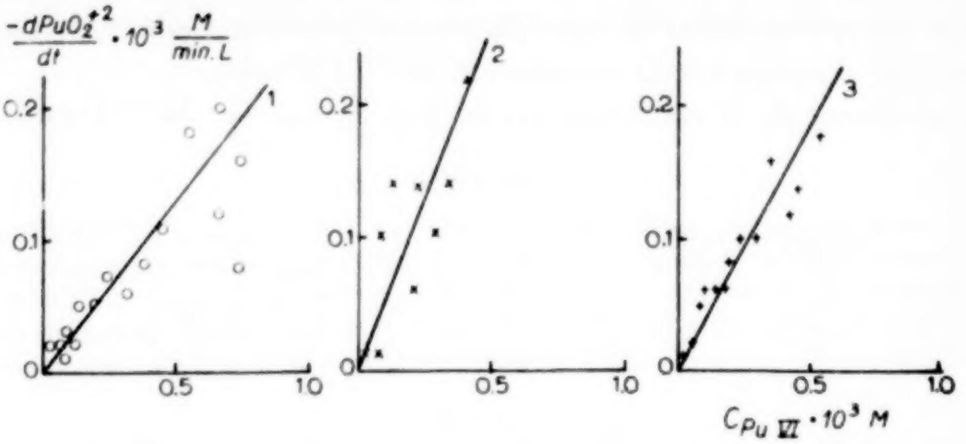

Fig. 9. Vitesses de réduction de Pu(VI) par le trilon B en excès. Concn. Pu = 0.0029 *M*; concn. trilon = 0.0035 *M*.

La pente des courbes permet de calculer les valeurs de K_1. Si l'on admet que la progression est linéaire, les valeurs des constantes de la vitesse de réaction K_1, peuvent être représentées par la Table I. Les valeurs de *K* sont calculées d'après l'équation (4).

TABLE I

CONSTANTES DE LA VITESSE DE REACTION (1)

Trilon B en excès et $NaClO_4$ absent, conc. trilon B = $3.5 \cdot 10^{-3}$ *M*

No. de la courbe dans la Fig. 9	*Concn. trilon B / Concn. Pu*	$K_1 \cdot 10^1$	$K \cdot 10^{-2}$
1	1.1	0.73	2.1
2	1.1	1.1	3.1
3	1.1	1.5	4.3
	moyenne	1	3

TABLE II

CONSTANTES DE LA VITESSE DE RÉACTION (1)

Concentration en trilon B dans la solution $NaClO_4$ relativement faible
Conc. Pu = $2.9 \cdot 10^{-3}$ *M*

No. de la courbe dans la Fig. 10	*Concn. trilon B · 10³M*	*Concn. trilon B / Concn. Pu*	$K \cdot 10^{-2}$
1	0.72	0.25	1.0
2	0.43	0.15	3.6
3	0.33	0.11	1.4
		moyenne	2

Lorsque la concentration en trilon B n'est pas suffisante, la vitesse de la réaction varie, elle est alors proportionnelle au produit de la concentration de PuO_2^{+2} par la concentration en trilon B. Dans ce cas les données expérimentales ont été calculées d'après les courbes des Fig. 1 et 6, elles sont représentées par la Fig. 10 et données dans la Table II.

L'angle des courbes (Fig. 10) nous donne immédiatement la valeur de K_1.

Les Tables I et II prouvent que la réaction (1) est une réaction du premier ordre par rapport à PuO_2^{+2} et trilon B; les valeurs des constantes sont très proches; elles ne dépendent pas du milieu (eau ou solution de $NaClO_4$ M).

La valeur moyenne de la constante est de $(2.5 \pm 1.0)\ 10^2\ M^{-1} \cdot l \cdot min^{-1}$.

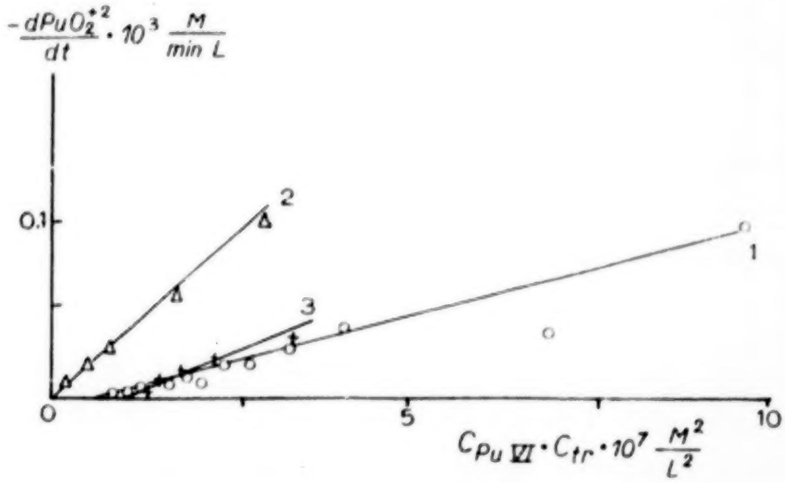

Fig. 10. Vitesses de réduction de Pu(VI) par le trilon B, (en quantités réduites). Concn. Pu = 0.0029 M. Courbe 1, concn. trilon B = 0.00072 M; courbe 2, concn. trilon B = 0.00043 M; courbe 3, concn. trilon B = 0.00033 M.

Le fait que la réaction de réduction de Pu(V) en Pu(IV) ne s'accomplit que lentement nous fait supposer que Pu(IV) ne se forme pas par réduction immédiate de Pu(V) avec le trilon B, mais plutôt par l'intermédiaire de la réaction de dismutation de Pu(V).

Pu(IV), ainsi obtenu, forme un complexe avec le trilon B, ce qui augmente considérablement la vitesse de dismutation. Il faut noter, que la vitesse de réduction de Pu(VI) par les produits d'irradiation α de l'eau[12] est beaucoup plus faible que les vitesses de réduction de PuO_2^{+2} par le trilon B, calculées ci-dessus. Pour une application analytique des ions complexes de Pu(V) et de Pu(IV) avec l'acide éthylènediaminotétracétique, il serait intéressant de faire une étude quantitative des complexes en question. Nous espérons la réaliser dans un travail ultérieur.

CONCLUSIONS

1. Dans les solutions de pH 3 à 5, le trilon B réduit Pu(VI) en Pu(V). Une molécule de trilon B réduit six ions PuO_2^{+2}.

2. La vitesse de la réaction de réduction de PuO_2^{+2} en Pu(V) par le trilon B est proportionnelle aux concentrations de PuO_2^{+2} et de trilon B; la réaction produit des ions H^+. La constante de la vitesse de réaction dans l'eau pure ainsi que dans la solution de $NaClO_4$ M à la température ordinaire est égale à $(2.5 \pm 1.0) 10^2 M^{-1} \cdot l \cdot min^{-1}$.

3. Les courbes du titrage conductimétrique des solutions de PuO_2ClO_4 par le

trilon B prouvent la formation du complexe, peu dissocié, de Pu(V) avec le trilon B, dans un rapport 1:1; cependant, le spectre d'absorption ne change pas.

4. La présence de trilon B dans la solution de Pu(V) produit une formation lente de Pu(IV).

5. Le spectre d'absorption de la solution du complexe de Pu(IV) avec le trilon B diffère du spectre de l'ion de Pu(IV) non complexé, qui existe dans des solutions plus acides.

RÉSUMÉ

Nous avons étudié les réactions des ions du plutonium dans les solutions de trilon B. Des mesures de densité optique ont montré qu'à pH = 3 à 5, Pu(VI) est réduit en Pu(V) par le trilon B. Le titrage conductimétrique d'une solution de plutonium(V) par le trilon B montre qu'il y a formation d'un complexe Pu(V)–trilon B (1:1). Pu(V) en solution, avec un excès de trilon B, passe en quelques jours à l'état d'un complexe Pu(IV)–trilon B.

SUMMARY

The behaviour of plutonium ions in a solution of trilon B was investigated. At pH 3–5 plutonium(VI) is reduced to plutonium(V) and a (1:1) complex of plutonium(V) and trilon B is formed. With excess trilon B a plutonium(IV)–trilon B complex is formed after some time.

ZUSAMMENFASSUNG

Es wurde das Verhalten von Plutonium-Ionen in einer Lösung von Trilon B untersucht: Bei pH 3–5 wird Plutonium(VI) zu Plutonium(V) reduziert und ein Komplex von Plutonium(V)–Trilon B (1:1) gebildet. Mit einem Ueberschuss von Trilon B bildet sich nach einiger Zeit ein Komplex von Plutonium(IV)–Trilon B.

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AMPEROMETRIC TITRATION OF BORON WITH FRUCTOSE

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The current use of boron as a key component in many synthetic preparations has increased the need of reliable methods for its determination. Although it is easy to convert boron to the borate form, it is often difficult to measure the borate ion concentration. Direct alkalimetric titration methods are not applicable because boric acid has such a low ionization constant. Direct gravimetric methods cannot be employed because there are no reagents that will selectively and quantitatively precipitate the borate ion.

The more or less classical method that is generally used for determining borate in aqueous solutions is based on complexing the borate with a polyhydric alcohol[1]. In this method the acidity of the solution is adjusted to pH 4 and a large excess of a polyhydric alcohol such as mannitol is added. The alcohol complexes the borate and releases an equivalent quantity of hydronium ions. The liberated hydronium ions are then titrated with standard alkali. This method when properly applied is accurate and features simplicity in technique. However, the method is not applicable in the presence of weak acids or bases. It is limited in that several milligrams of boron are required for a reasonably accurate titration.

The more recent developments have for the most part been modifications of the classical method or the development of new colorimetric procedures. The colorimetric methods although very sensitive are often subject to involved manipulations to offset such factors as unstable reagents, time dependent color development, contamination by trace impurities, etc.

Heyrovský and Smoleř[2] found that fructose gives a well defined polarographic wave with the DME in a 0.1 *M* lithium chloride solution in both a neutral and an alkaline medium.

Jambor and Kisban[3] demonstrated that boric acid depresses the polarographic wave height of glucazone without affecting its half wave potential. A similar effect was noticed in the polarography of fructose. In this case the wave height of the fructose itself was depressed by the presence of borate. Since fructose exhibits a well defined polarographic wave, an investigation has been made to see if this phenomenon could be utilized as a basis for a quantitative method to determine boron. It was found that the amount that the wave is depressed is related to the concentration of boron but the relationship is not directly proportional. However, if the borate is titrated amperometrically with standard fructose to a preestablished current value the relationship between the titer and boron concentration is a direct proportion. The method described is based upon this amperometric technique.

APPARATUS

Leeds and Northrup Electro-Chemograph Type E, was used in this study. Any other polarographic instrument capable of applying a potential of —2.05 V and measuring current in the μA range might be used.

The polarographic Cell Assembly shown in Fig. 1 was employed. It was equipped with a micro buret graduated in units of 0.002 ml. A silver-silver chloride reference electrode and a dropping mercury electrode were used. The constant temperature bath maintained the temperature within ± 0.1°.

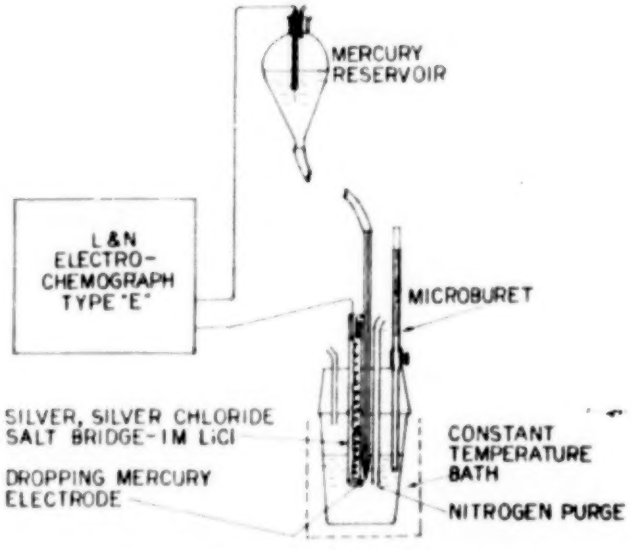
MERCURY RESERVOIR
L&N ELECTRO-CHEMOGRAPH TYPE "E"
MICROBURET
SILVER, SILVER CHLORIDE SALT BRIDGE-1M LiCl
DROPPING MERCURY ELECTRODE
CONSTANT TEMPERATURE BATH
NITROGEN PURGE

Fig. 1. Polarographic assembly.

PREPARATION OF REAGENTS

Fructose (0.1 *M*): dissolve 18.012 g of reagent grade D(-)levulose in water and dilute to one l. Standard borate (0.2 mg of boron per ml): dissolve 1.142 g of boric acid in water and dilute to one l. Lithium chloride–lithium hydroxide (1.0 *M* and 0.1 *N*): dissolve 42.4 g of lithium chloride and 4.2 g of lithium hydroxide mono-hydrate in water and dilute to one l. Lithium hydroxide (0.1 *N*): dissolve 4.2 g of lithium hydroxide monohydrate in water and dilute to one l. Hydrochloric acid (0.1 *N*): dilute 8.3 ml of conc. hydrochloric acid to one l with water. Phenolphthalein indicator: dissolve 1 g of indicator in 50 ml of ethyl alcohol and add 50 ml of water.

CALIBRATION CURVE

To a series of 25-ml volumetric flasks add the following volumes of standard borate solution, 0, 1, 2, 3, 4, 5 ml. Treat each solution in the following manner:

Add 1 drop of phenolphthalein indicator solution and neutralize by the dropwise addition of 0.1 *N* lithium hydroxide. Add 2.5 ml of the lithium chloride–lithium hydroxide electrolyte and dilute to the mark with water. Pipet 20 ml of the solution into a polarographic cell and measure the pH with a pH meter using the glass–calomel electrode system. If the pH differs from 12 by more than 0.1 units, adjust to that value by the addition of either 0.1 *N* hydrochloric acid or lithium hydroxide, from a 1 ml Mohr pipet. Record the exact volume of solution used in making this adjustment. Attach the cell to the polarographic assembly and purge with nitrogen for a period of 5 min. Record the height of the mercury column and the cell temperature. The calibration curve will be valid only for these conditions of temperature and mercury height. Set the current sensitivity dial so that full scale deflection corresponds to three μA and with an applied potential of —2.05 V, record the value of current flowing through the circuit. Add a series of small increments of 0.1 M fructose from the buret, purging with nitrogen for 1 min between each addition, and record the corrected current values corresponding to each incremental addition. All observed current values after the initial reading must be corrected because of dilution by the following equation:

$$I_{\text{corr.}} = \frac{(I_{\text{obs.}})\,(V_N + V_t)}{20}$$

where $I_{\text{corr.}}$ = corrected current (μA), $I_{\text{obs.}}$ = observed current (μA), V_N = volume of solution required to adjust pH (ml), V_t = volume of titrant added (ml).

Make a plot of diffusion current against volume of titrant and record the value of titrant corresponding to a current increase of 1.5 μA as the end-point of the titration.

Subtract the volume of titrant corresponding to the end-point of the blank (solution containing no boron) from the end-point values of the other solutions. Prepare the calibration curve by plotting the titration differences against the mg of boron in each standard solution.

PROCEDURE

In a 25-ml volumetric flask, neutralize to a phenolphthalein end-point a solution containing from 0.1 to 2 mg of boron by the addition of 0.1 N lithium hydroxide or hydrochloric acid. If the volume of sample solution is too great, make the solution alkaline with lithium hydroxide and evaporate in boron free glassware to a volume of about 15 ml and transfer to a 25-ml volumetric flask. Add 2.5 ml of the lithium chloride–lithium hydroxide electrolyte and dilute to the mark with water. Pipet 20 ml of the resulting solution into a polarographic cell and follow the procedure described for titrating the standard solutions used in the preparation of the calibration curve. Determine a reagent blank for each set of samples. Using the difference in titer between the sample and reagent blank, determine the boron concentration from the calibration curve. Calculate the percent boron in the sample with the following equation:

$$X = \frac{(M)\,(100)}{(1000)\,(W)}$$

Where X = % boron in sample. M = mg of boron from the calibration curve. W = weight of sample analyzed.

RESULTS AND DISCUSSION

A polarogram of fructose at 30° in a 0.1 N lithium chloride adjusted to a pH of 12 with lithium hydroxide is shown in Fig. 2. The fructose wave starts in the vicinity of —1.80 V and reaches a limiting current at —2.05 V. The value of the limiting current increases with pH and at pH values greater than 9.5 is directly proportional to the fructose concentration. A plot of limiting current against concentration at pH 12 is shown in Fig. 3. These results show that both temperature and pH must be controlled in this system.

It was found that the presence of the borate ion depresses the limiting current of the fructose wave without significantly effecting the half wave potential. Fig. 4 shows the depression of the polarographic wave of a $6.6 \cdot 10^{-4}$ molar solution of

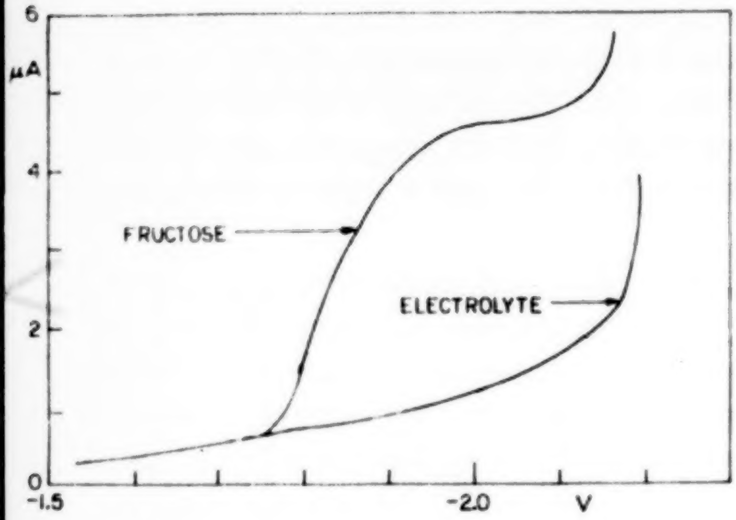

Fig. 2. Polarogram of fructose.

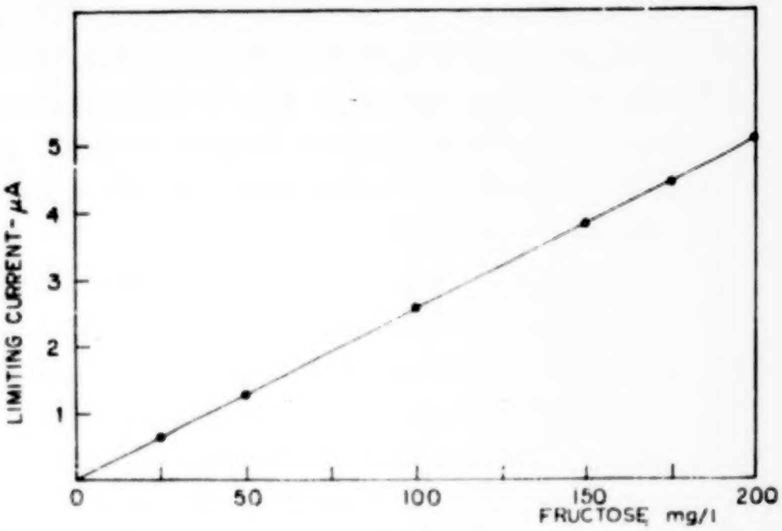

Fig. 3. Relationship of fructose concn. to limiting current.

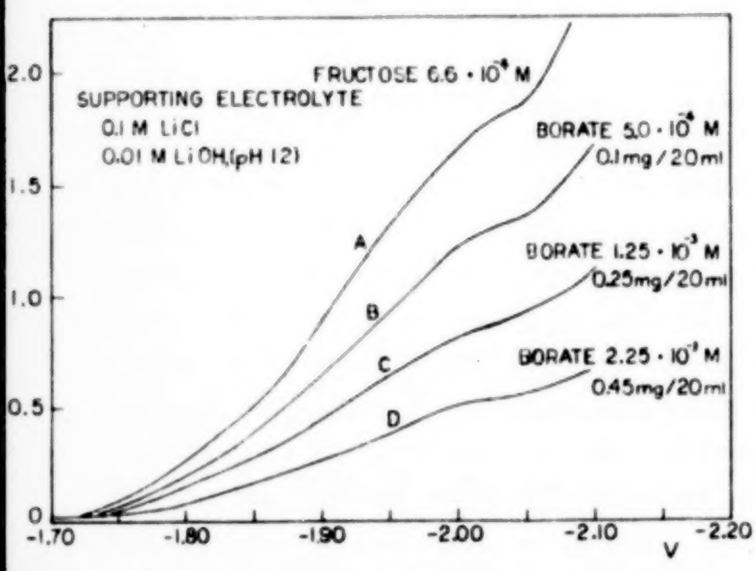

Fig. 4. Effect of borate on the fructose polarogram. Polarogram A $6.6 \cdot 10^{-4}$ *M* fructose. Polarogram B $6.6 \cdot 10^{-4}$ *M* fructose, $5 \cdot 10^{-4}$ *M* borate. Polarogram C $6.6 \cdot 10^{-4}$ *M* fructose, $1.25 \cdot 10^{-3}$ *M* borate. Polarogram D $6.6 \cdot 10^{-4}$ *M* fructose, $2.25 \cdot 10^{-3}$ *M* borate.

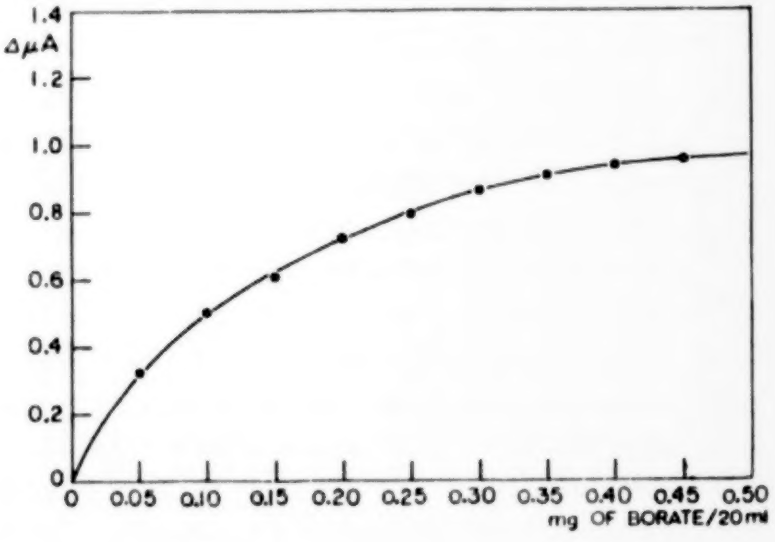

Fig. 5. Change in limiting current *vs.* borate concentration.

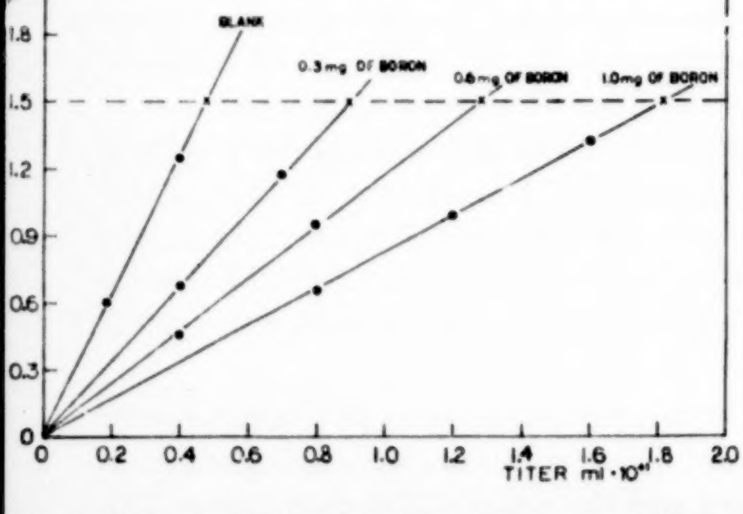

Fig. 6. Amperometric titrations of borate solutions with 0.1 *M* fructose at —2.05 V.

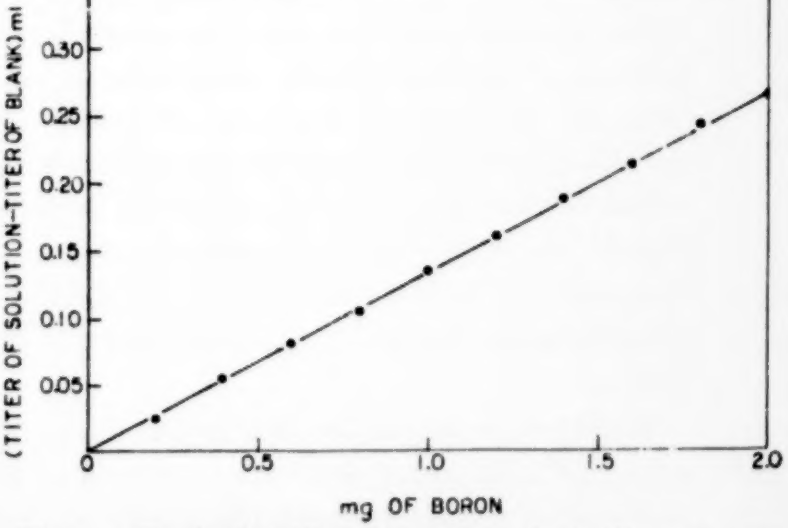

Fig. 7. Typical calibration curve (net titer *vs.* mg of boron).

fructose at pH 12 caused by the presence of various amounts of boron. The amount of depression is not directly proportional to the boron concentration. A plot of this relationship is shown in Fig. 5. An analytical method developed with this relationship as its basis would have a limited range in that at higher concentrations the sensitivity is decreased. To offset this condition one would have to make tedious dilutions, readjustments of pH, etc.

In order to examine the amperometric technique a series of solutions was prepared containing known amounts of boron in a 0.1 N lithium chloride solution adjusted to a pH of 12 with lithium hydroxide. Each solution was placed in a polarographic cell and titrated amperometrically with a 0.1 N fructose solution at a potential of —2.05 V. After correcting for the volume of titrant added, a plot of current against ml of titrant was made, Fig. 6. For each titration the plot of current against titrant is a straight line differing only by its respective slope. It is noted that at a constant current value such as 1.5 μA that the difference between the volume of titrant corresponding to the blank and of the standard is directly proportional to the concentration of boron. This proportionality is shown in the plot of Fig. 7.

Since the amperometric titration is carried out at an applied potential of —2.05 V, all polarographically active cations present in even small concentrations with the exception of lithium will interfere. The interference is due to the reduction of the cations at more positive potentials than the fructose causing a considerable quantity of current to flow through the circuit. This makes the measurement of the current due to the fructose highly inaccurate. However this interference may be removed very conveniently by passing the sample through the hydrogen form of a cation-exchange resin. The ion-exchange procedure has been described in detail by MARTIN AND HAYES[4]. The applicability of this procedure was tested by preparing several standard boron solutions containing various polarographically active cations and passing them through the exchange resin before making the amperometric titrations. The results are shown in Table I.

Commonly occurring anions such as chloride, iodide, bromide, phosphate, and carbonate do not interfere. Bromate and iodate ions do interfere because they are reduced at more positive potentials than fructose. Interference from these anions may be eliminated by passing sulfur dioxide gas through the sample while in the alkaline form, thus reducing the anions to bromide and iodide respectively.

The method has been used successfully in our laboratories to determine the boron content of new synthetic preparations of compounds such as BPI_2 and adducts from the reaction of tripropyl phosphine and diborane. The general procedure consisted of decomposing the sample by sodium peroxide fusion and passing the resulting solution through a cation-exchange resin to remove the sodium. An aliquot of the eluant was tested by the proposed method. In the case of BPI_2 a portion of the iodide was oxidized to the iodate state during the fusion process. This necessitated reducing the iodate to iodide by purging with sulfur dioxide prior to the amperometric titration.

In order to obtain an idea of the accuracy of the method a series of solutions were prepared containing known quantities of boron. These solutions were analyzed over a period of a month using the above procedure and the same calibration curve. The results of the analysis indicating an accuracy of about ± 0.01 mg are listed in Table II.

TABLE I

ACCURACY OF THE ANALYSIS AFTER TREATMENT BY ION EXCHANGE

Cations originally present mg/25 ml	*Boron present mg/25 ml*	*Boron found mg/25 ml*
Na^+ (40)	1.00	1.02
Na^+ (40)	0.50	0.49
Zn^{+2} (20)	1.00	1.00
Mg^{+2} (20)	1.00	0.98
Ca^{+2} (20)	1.00	1.01
Cu^{+2} (20)	1.00	1.00
Cu^{+2} (40)	0.50	0.51

TABLE II

ACCURACY OF TITRIMETRIC PROCEDURE

Boron present mg/25 ml	*Boron found mg/25 ml*	*Deviation*
0.05	0.05	—
0.10	0.09	−0.01
0.35	0.36	+0.01
0.49	0.50	+0.01
0.74	0.74	—
0.98	0.98	—
1.10	1.12	+0.02
1.42	1.42	—
1.67	1.66	−0.01
1.80	1.81	+0.01
1.90	1.90	—
2.00	1.98	−0.02

S.D. ± 0.007

Although we have not tested it, the method should be applicable to those procedures requiring that the boron be distilled from a sulfuric acid–methyl alcohol solution as methyl borate. The distillate would be collected in a lithium hydroxide solution and titrated directly.

SUMMARY

Aqueous solutions of borate can be titrated amperometrically with standard fructose solutions. This procedure may be used to determine the boron content of various types of samples after conversion of the boron to the borate form. The method is based upon the observation that the polarographic wave of fructose in a 0.1 *M* LiCl, 0.01 *N* LiOH solution is depressed by the presence of borate ions. Under the prescribed conditions the method is sensitive to a few hundredths of a milligram of boron. The few commonly occurring interferences can be conveniently removed prior to the titration.

RÉSUMÉ

Les auteurs proposent une méthode de titrage ampérométrique des borates au moyen d'une solution étalon de fructose. Elle est basée sur la réduction de l'onde polarographique du fructose par addition d'un borate. On peut ainsi déterminer la teneur en bore de divers types d'échantillon après transformation en borate.

ZUSAMMENFASSUNG

Borate können amperometrisch mit Standard-Fructoselösungen titriert werden. Die Methode beruht auf der Beobachtung, dass die polarographische Kurve von Fructose durch Borat-Ionen abgeflacht wird.

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THE DETERMINATION OF URANIUM BY CATHODE-RAY POLAROGRAPHY

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INTRODUCTION

The determination of uranium by conventional polarography is an accepted and widely used technique as may be seen from the numerous papers on the subject in recent years[1]. Recently MILNER AND NUNN[2] made a study of this determination using a square wave polarograph, but the only published application of cathode-ray polarography to this determination appears to be that of TUCKER[3].

In view of the inherently greater sensitivity, speed of operation, and discrimination against interfering reductions of the C.R. polarograph as compared with conventional instruments, it was decided to develop a method applicable to the C.R. instrument.

THEORETICAL

In contrast to normal polarography in which a steady or average diffusion current is measured, the C.R. polarograph indicates the change in current, produced by the application to the dropping mercury electrode of a fairly rapid potential sweep, linear with respect to time.

The complexity of the reactions occurring at the dropping mercury electrode during the polarography of uranium solutions is such that in view of the different mode of operation of the two polarographs, the method for the determination of uranium described by SHALGOSKY[4] is inapplicable to the latter instrument.

The formal potentials of the various oxidation states of uranium in 1 M perchloric acid at 25° are[5,6].

$$\begin{tikzcd}
U \arrow[r, dash, "-1.80\ V"] & U^{+3} \arrow[r, dash, "-0.63\ V"] & U^{+4} \arrow[r, dash, "+0.58\ V"] \arrow[rr, dash, bend right, "+0.32\ V"'] & UO_2^{+} \arrow[r, dash, "+0.063\ V"] & UO_2^{+2}
\end{tikzcd}$$

Experimentally it is found that the U(IV)/U(III) and U(VI)/U(V) couples are reversible, whilst the U(V)/U(IV) and U(VI)/U(IV) couples are irreversible. This is in agreement with a criterion for reversibility that no covalent metal-oxygen bonds are formed or broken during reduction–oxidation.

Apart from the complexity of polarograms resulting from the possible production of the three waves corresponding to U(VI) → U(V), U(V) → U(IV), and U(IV) → U(III), the primary reduction product U(V) is capable of disproportionation *viz.:*

$UO_2^{+} + H^{+} \longrightarrow UOOH^{+2}$

$UO_2^{+} + UOOH^{+2} \longrightarrow UO_2^{+2} + UOOH^{+}$ (Rate determining step)

$UOOH^{+} \longrightarrow$ Stable U(IV) species.

Although this mechanism, proposed by **Kern and Orlemann**[7], involving a proton transfer has been challenged as a result of the work of **Duke and Pinkerton**[8], the rate of disproportionation is first order with respect to the hydrogen ion concentration and second order with respect to the U(V) concentration. Additionally, the rate of disproportionation is greatly increased in the presence of anions which form strong complexes with U(IV) species (*e.g.* SO_4^{-2} and F^-)[9].

Using an ordinary polarograph, the method described by **Shalgosky**[4], in which a perchloric–sulphuric–tartrate supporting electrolyte is used, yields *n* values of about 1.8 down to a uranium concentration of approximately 10^{-4} *M*. The drop time of the electrode is sufficiently long for conditions of apparent equilibrium to be obtained and for *n* to approach the value of 2 for the U(VI) → U(IV) reduction.

In the case of the C.R. polarograph the criterion for the production of a well defined wave is that the reduction should be rapid and reversible, and, in the case of a reduction followed by a chemical reaction leading to further reduction, that the rate of the chemical reaction must be very rapid in comparison with the rate of potential sweep applied to the dropping mercury electrode. From the ill-defined shape of the wave on the C.R. polarograph this latter condition does not appear to be fulfilled in the case of the disproportionation of U(V) in the sulphuric–tartrate base mentioned above.

However, in the presence of fluoride ions, the rate of disproportionation of U(V) is very fast[9], and on the C.R. instrument the wave height thus obtained is about 80% greater than that expected for a one electron reduction, but owing to the deleterious effect of fluoride ions on the dropping mercury electrode, and the failure hitherto to produce a permanent electrode in plastic, the method is of little use in practice.

In order therefore to avoid the complications and difficulties arising from complex formation in the supporting electrolyte, a study was made of the behaviour of uranium in a relatively non-complexing base solution, *viz.* perchloric acid, using both a conventional and a C.R. polarograph.

EXPERIMENTAL

Apparatus, reagents and experimental conditions

Cambridge Instrument Co. pen recording polarograph. Maximum sensitivity $2.5 \cdot 10^{-3}\ \mu A \cdot mm^{-1}$. Capillary characteristic $1.92\ mg^{\frac{2}{3}} \cdot sec^{-\frac{1}{2}}$ in 1 *M* potassium chloride with no applied potential. Cathode Ray polarograph. Capillary characteristic. Weight of one drop (W) = 6.0 mg in 1 *M* potassium chloride with no applied potential.

Half wave potentials refer to the mercury pool anode, unless specified against the saturated calomel electrode (S.C.E.). In the latter case they were measured between the dropping mercury electrode and the S.C.E. via a $NaClO_4$–agar salt bridge under conditions in which "no current" was drawn in the measuring circuit.

Solutions were deoxygenated with high purity ("white spot") nitrogen, and polarographed at 25 ± 0.1° using a mercury pool as anode.

A standard uranium solution was prepared by dissolving the pure metal in nitric acid and evaporating to fuming after the addition of perchloric acid. The final solution was 0.100 *M* with respect to uranium, and 1 *M* with respect to perchloric acid. Additional uranium solutions were prepared by dilution of this standard with perchloric acid, such that the acidity was maintained at 1 *M*.

When required, a 0.1% solution of B.D.H. peptone, containing 0.2% of redistilled phenol as preservative was used as a "maximum suppressor", this solution being diluted 100 fold in use.

Reagents were of AnalaR or equivalent quality, and in particular the perchloric and hydrochloric acids used in the preparation of the more dilute ($\leqslant 4 \cdot 10^{-5}$ *M*) uranium solutions were "lead free" (Pb $\ngtr$ 0.005 p.p.m.).

Redistilled water was used throughout.

Effects of uranium concentration and of acidity

In the initial experiments the effects of variations in the concentrations of uranium and acidity were examined. Except for Series 1 and 2, the ionic strength was maintained at 1.0 by the addition of sodium perchlorate.

The results of these experiments are given in Table I.

In considering alternative acid supporting electrolytes, sulphuric acid is, as already mentioned, unsatisfactory for use with the C.R. instrument. The use of nitric or hydrochloric acids involves control of the acidity or, more specifically, control of the concentration of nitrate or chloride ion, because of their effect on the rate of disproportionation of U(V) owing to their complexing of U(IV) species.

TABLE I

EFFECT OF URANIUM CONCENTRATION AND ACIDITY

Series	*Concentration of U in mM/l*	*Concentration of H^+ in moles/l*	*Step height in mm*[a]	
			Pen recording polarograph	*C.R. polarograph*
1	4.00	5.0	7420	13,500
	0.40		660	1,050
	0.040		54	105
2	4.00	2.0	6750	10,000
	0.40		600	1,070
	0.040		50	97
3	4.00	1.0	6100	10,000
	0.40		520	1,000
	0.040		50	100
4	4.00	0.50	5700	10,000
	0.40		510	950
	0.040		50	100
5	4.00	0.10	5250	10,000
	0.40		517	1,000
	0.040		42	95
6	4.00	$1.26 \cdot 10^{-2}$	5170	9,500
	0.40		510	975
	0.040		41	85
7	4.00	$1.0 \cdot 10^{-3}$	5170	9,500
	0.40		480	1,000
	0.040		42	105

[a] The step heights are those which would be obtained (a) using the maximum sensitivity of the Cambridge instrument (b) using 1/20 of the maximum sensitivity of the C.R. instrument.

Interferences

Copper, lead, antimony, arsenic, tin, molybdenum, bismuth and vanadium were noted as possible interfering elements in the determination of uranium, and their behaviour in 1:1 ratio to uranium in a *N* $HClO_4$ – 0.01 *N* HCl supporting electrolyte was examined.

Mo causes serious interference and must be removed. Sb and V caused slight interference by distortion of the base of the uranium wave.

Bi when present as bismuth perchlorate, caused no interference, but the addition of bismuth in the form of a solution in hydrochloric acid produced interference. This is attributable to the complexing of bismuth by chloride ion and the reduction of this complex at a more negative potential than that of the bismuthyl ion. Pb, As, Sn caused no interference, their reduction waves occurring well after that due to uranium.

Cu caused no interference, the reduction wave preceded the uranium wave by a substantial amount.

Following the observation by LEWIS AND OVERTON[10] "that uranium gives a wave in acid tartrate solution which is removed from the copper wave" it may have been inferred by other workers that the addition of tartrate was necessary to separate the uranium and copper waves in other media.

Measurements were therefore made of the half-wave potentials of uranium, copper and lead in the proposed supporting electrolyte and following the addition of tartrate. The results of these measurements are shown in Table II.

TABLE II

HALF-WAVE POTENTIALS

Element	*Medium*	*$E_{\frac{1}{2}}$ V vs. S.C.E.*	
Uranium	(a) 1 *N* $HClO_4$ 0.01 *N* HCl	— 0.200	± 0.005
	(b) 1 *N* $HClO_4$ 0.01 *N* HCl 0.05 *M* Sodium tartrate	— 0.195	
Copper	as in (a) above	— 0.010	± 0.005
	as in (b) above	— 0.000	
Lead	as in (a) above	— 0.420	± 0.005
	as in (b) above	— 0.420	

Calibration curves were prepared over the range $2 \cdot 10^{-6}$–$4 \cdot 10^{-3}$ *M* uranium in the case of the C.R. instrument and $4 \cdot 10^{-5}$–$4 \cdot 10^{-3}$ *M* for the pen recorder, and checks made of the precision of the proposed procedure, which in common with most methods for the determination of uranium is best applied after a preliminary separation.

DISCUSSION

From the results shown in Table I, it is apparent that the height of the uranium wave is relatively insensitive to changes in acidity around the 1 *M* level, and this is of great practical convenience. At pH values greater than 1 the results on the Cathode Ray instrument were often unsatisfactory owing to the splitting of the wave into two parts.

In order to establish a stable and reproducible anode potential it is customary to add chloride ions to the supporting electrolyte, and the addition of hydrochloric acid to give a concentration of 0.01 *M* fulfils this requirement.

Whilst the suggested concentration is uncritical to say ± 100%, it should not be permitted to reach 0.1 *M*, or higher, since for example in the presence of copper the stabilisation of cuprous ions by chloride complexing will result in the copper reduction proceeding in two steps and to the reduction potential becoming sufficiently negative to interfere with the uranium wave. A similar situation arises in the presence of bismuth.

In solutions containing these larger amounts of chloride, this interference can be overcome by lowering the acidity to pH 1–2 and adding tartrate. Since the reaction between cupric and tartrate ions is considered to involve the replacement of hydroxyl group hydrogens[11,12] as well possibly as attachment through carboxylate groupings, the degree of complex formation will obviously be very pH-dependent. It is not surprising therefore that, (as is shown in Table II) the addition of tartrate has an insignificant effect on the values of the half-wave potential at an acidity of 1 *M*.

The two acids are available in a state of high purity. Alternatively they can readily be further purified by distillation, and in the case of hydrochloric acid the isopiestic[13] method is applicable.

CONCLUSIONS

An electrolyte 1 *M* with respect to perchloric acid and 0.01 *M* with respect to hydrochloric acid forms a very satisfactory base for the determination of uranium by either conventional or cathode-ray polarography.

Accurate control of the acidity of the base solution is unnecessary.

The only element causing serious interference is molybdenum.

For the C.R. polarograph the calibration is linear over the range $2\cdot10^{-6}$–$4\cdot10^{-3}$ *M* uranium. At a uranium concentration of $4\cdot10^{-5}$ *M* the coefficient of variation of the results from the Cambridge Polarograph is 1.8% and that for the Cathode Ray is 1.5%. At a uranium concentration of $4\cdot10^{-4}$ *M* these figures are 1.8% and 1.3% respectively.

The method is particularly suited to the determination of uranium, following separation procedures such as those described by WILD[14] or MAECK *et al.*[15].

ACKNOWLEDGEMENTS

The authors wish to thank Mr. H. I. SHALGOSKY for valuable discussions, and Mrs. S. BROWN who carried out much of the experimental work.

SUMMARY

The determination of uranium in the concentration range $2\cdot10^{-6}$–$4\cdot10^{-3}$ *M* has been studied by using both conventional and cathode-ray polarography. The preferred supporting electrolyte is 1 *M* perchloric acid, molybdenum is the only element which will cause serious interference at levels of the same order as that of the uranium.

RÉSUMÉ

Une étude a été effectuée sur le dosage de l'uranium, par polarographie ordinaire et par polarographie à rayon cathodique. On propose l'acide perchlorique comme électrolyte de base.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Uran durch gewöhnliche oder Kathodenstrahlen-Polarographie in Gegenwart von Perchlorsäure.

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THE DETERMINATION OF ORGANIC NITRO, NITROSO AND AZO COMPOUNDS WITH COPPER

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INTRODUCTION

An excellent review of the various methods for the quantitative determination of nitro groups has been given by BECKER AND SHAEFER[1]. Most of these methods involve the reduction of the nitro group with a known excess of a strong reducing agent such as titanous, stannous, or chromous ion followed by back-titration, after the reaction is complete, with a standard solution of an appropriate oxidizing agent. These methods are not convenient for a single or occasional analysis since two standard solutions must be prepared; one of these, the reducing agent, is commonly oxygen sensitive and requires storage of stock solutions under an inert atmosphere and frequent standardizations.

In 1950 VANDERZEE AND EDGELL[2] proposed an indirect gravimetric method for the determination of aromatic nitro compounds which was based on the reduction of the nitro group to the amine in acidic solution with an excess of metallic tin. From the loss in weight of the tin, the amount of nitro compound could be calculated. The procedure has the advantage that no standard solutions are required and only commonly available equipment is used. Under ideal conditions the accuracy was found to be ± 0.5%. These authors, however, point out several difficulties with the procedure. Large errors result from oxidation of the metallic tin by air and by excess hydrogen ion. VANDERZEE AND EDGELL state that the initial acid concentration should be adjusted so that the final concentration, after reaction, is approximately 0.15 *M*; the concentration of alcohol solvent should be minimized to reduce errors; and sufficient nitro compound to cause reaction of *ca.* 0.7 g of tin should be used since the value of the blank is relatively large. As a result, careful attention to experimental details is required. Certain compounds, *i.e.*, *p*- and *m*-iodonitrobenzene, *m*-nitrobenzaldehyde and 1,3,5-trinitrobenzene, were found to give errors as large as 6–10% even under ideal conditions.

The procedure given below is similar, in principle, to the method of VANDERZEE AND EDGELL. However, many of the difficulties associated with the use of tin have been eliminated by the choice of a reducing metal which is not oxidized by hydrogen ion. Copper metal was chosen because of its availability in pure form and because it is not oxidized by protons. The concentrations of the acid and the organic solvent have no appreciable influence on the analytical results.

EXPERIMENTAL

Apparatus

Reactions were carried out in a 200-ml round-bottom flask fitted with a reflux condenser by means of a ground-glass joint. A two-hole rubber stopper, through which was inserted a glass tube for carbon dioxide delivery, was placed in the top of the reflux condenser. Alternatively, small pieces of "dry ice" could be added from time to time through the condenser to maintain an inert atmosphere above the reaction mixture.

Reagents

Reagent-grade absolute ethanol (U.S. Industrial Chemicals Co., New York) was used without further purification. Diethylene glycol dimethyl ether (Ether 141, Ansul Chemical Co., Marinette, Wisc.) was distilled from metallic copper. After long contact of the ether with air, destruction of peroxides by distillation from dilute sulfuric acid saturated with ferrous sulfate may be desirable. These solvents were deaerated before use by bubbling with carbon dioxide. Electrolytic copper foil (Allied Chemical and Dye Corp., New York, 0.002 in thick) was cut into pieces approximately 1 cm square. These were bent into a cylindrical form to facilitate drying. The copper was washed with dilute sulfuric acid, rinsed with deaerated water and deaerated reagent-grade acetone, dried in a filter flask under a stream of carbon dioxide, and stored under vacuum. The copper could be used for successive determinations provided air oxidation between determinations was avoided and no insoluble coating was formed on the surface during reaction. Most of the compounds determined were Eastman "white label" reagents which had been recrystallized according to standard techniques. The melting points were taken and were in close agreement with literature values.

Analytical procedure

Twenty ml of ethanol or Ether 141 and 20 ml of *ca.* 6 *N* sulfuric acid were added to the reaction flask. Deaeration of the mixture was carried out by addition of small pieces of "dry ice". Sufficient nitro compound to cause reaction of 0.5 to 1 g of copper metal was dissolved in the solvent and 6 to 15 g of clean, dry copper were added to the reaction flask. The mixture was refluxed for 1 to 2 h while a slow stream of carbon dioxide was passed through the condenser. Small pieces of "dry ice" may be added during the reflux period as a substitute for the gas, if desired.

After completion of the reaction, the liquid was decanted from the flask. Five or six rapid rinses of the copper with deaerated water were followed by three rinses with deaerated acetone. The copper was dried under vacuum and weighed. The loss in weight of copper is related to the amount of nitro compound present by the equation.

$$3Cu + ArNO_2 + 7H^+ = 3Cu^{+2} + ArNH_3^+ + 2H_2O \qquad (1)$$

Blanks were run along with the samples and varied from 1.2 to 18 mg copper depending upon care used in excluding oxygen from the reaction vessel and reagents.

RESULTS

The results obtained for several compounds are given in Table I. Accuracy and precision is of the order of 0.5%.

The reaction time given is not necessarily the shortest time required for quantitative reaction. Most reductions are complete after 1–1.5 h. Reduction generally proceeds faster in Ether 141 than in ethanol because of the higher reflux temperature. As a generalization, compounds with three nitro groups may be reduced faster than those with two, which react faster than those with one. Aliphatic nitro compounds are much more resistant to reduction than aromatic compounds and require an inconveniently long reaction time.

TABLE I

DETERMINATION OF VARIOUS NITRO, NITROSO, AND AZO COMPOUNDS

Solvent A: 20 ml ethanol, 20 ml 6 *N* H_2SO_4; Solvent B: 20 ml Ether 141, 20 ml 6 *N* H_2SO_4

Compound	*Reaction time, h*	*Solvent*	*Average % recovery and S. D.*
m-chloronitrobenzene	2	A	100.7 ± 0.3
m-nitrobenzaldehyde	2	A	101.5 ± 0.7
m-nitrobenzonitrile	2	A	100.9 ± 1.2
p-nitrobenzoic acid	2	A	100.3 ± 0.7
o-nitrophenol	2.5	A	100.8 ± 0.7
m-dinitrobenzene	2	A	100.1 ± 0.9
m-dinitro-*o*-cresol	2.5	A	100.7 ± 0.4
2,4-dinitrotoluene	1.5	B	100.4 ± 0.1
2,4,6-trinitrotoluene	1	B	100.3 ± 0.3
picric acid	1	B	99.8 ± 0.2
1,3,5-trinitrobenzene	1	B	101.1 ± 0.6
4-dimethylaminoazobenzene	2.5	A	98.7 ± 0.6
Azobenzene-4-carboxylic acid	2.5	A	99.9 ± 0.7
p-nitrosodiethylaniline	1	B	98.9 ± 0.4
tri(hydroxymethyl)nitromethane	22	A	99.8
tri(chloromethyl)nitromethane	22	A	100.3
m-iodonitrobenzene	1.5–2	A,B	104.2 ± 1.3

A series of determinations of 2,4-dinitrotoluene was made using concentrations of sulfuric acid varying from 2 to 4 *N*. Although the reaction apparently proceeds more slowly at lower acid concentrations, essentially quantitative results were obtained in each case and precise control of acid concentration is not necessary. This is a definite advantage of copper metal over tin as a reducing agent.

Two of the compounds, 1,3,5-trinitrobenzene and picric acid, caused an insoluble coating to form on the copper during the reflux period. Reduction of sample size to *ca.* 0.2 g decreased interference from this source. In the determination of styphnic acid, 2,4,6-trinitroresorcinol (not shown in the table), sufficient coating was formed with even a 0.2-g sample to lower the results to 94.5% of the theoretical value. No suitable solvent for this coating was found.

Since the performance of a nitroso compound was of interest, *p*-nitrosodiethylaniline was studied. Reduction was rapid, requiring only 1 h reflux when Ether 141 was used as the organic solvent. The result (assuming 4 equivs. per mole), corrected for a reaction mixture blank of 2.8 mg, was 98.9 ± 0.4%. The blank was determined by refluxing the amine reaction mixture with a weighed amount of copper for the same length of time used for the original reaction.

LIMITATIONS AND INTERFERENCES

Several workers have shown that reduction products other than the simple amines are formed in the reduction of α-nitronaphthalenes with titanous ion[3] and with tin[4] in the presence of hydrochloric acid. The reaction of copper metal with both 1-nitronaphthalene and 1-nitro-2-methylnaphthalene was found to give consistently low results based on the normal six equivalents per nitro group reduced. The reduction products were isolated in order to determine the presence of products other than the simple amines. After refluxing 1-nitronaphthalene for 6 h with ethanol as the organic solvent, the reaction mixture was allowed to cool. A white crystalline compound, which was the sulfate salt of 4-ethoxy-1-naphthylamine, separated.

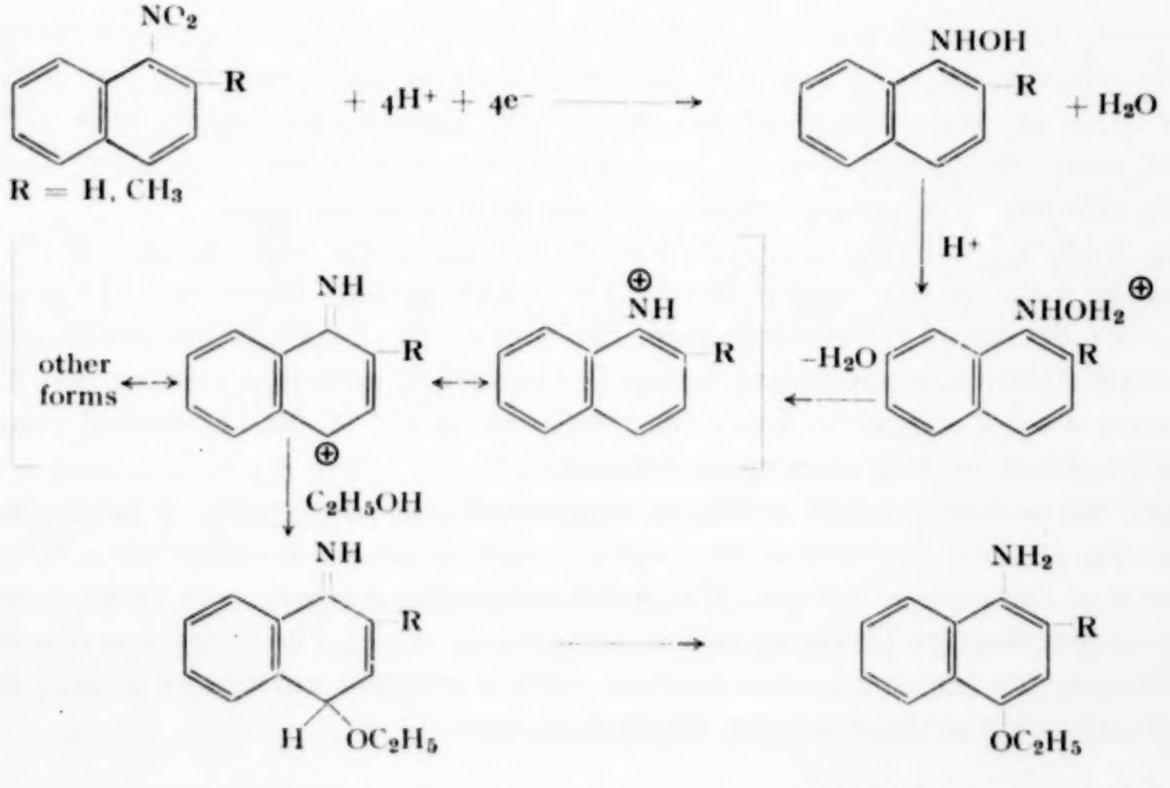
Anal.: Calculated for $(C_{12}H_{14}NO)_2SO_4$: C, 61.00%; H, 5.97%; N, 5.93%. Found: C, 61.35%; H, 5.94%; N, 5.61%.

The benzamide of the free amine melted at 213–14°. The literature[5] reports the melting point of 4-ethoxy-1-naphthylbenzamide as 214–15°.

An acidic aqueous ethanol solution of 2-methyl-1-nitronaphthalene was reduced by refluxing with copper metal for 12 h. Excess ethanol was removed by distillation, and the benzamide of the reduction product was prepared by the Schotten-Baumann method. The product was isolated by chromatography using a benzene–ether eluent with 100–200 mesh Florisil (Floridin Co., Tallahassee, Fla.). The melting point of the benzamide, 4-ethoxy-2-methyl-1-naphthylbenzamide, was 180.5–181.0°.

Anal.: Calculated for $C_{20}H_{19}NO_2$: C, 78.66%; H, 6.27%; N, 4.59%. Found: C, 78.39%; H, 5.93%; N, 4.76%.

The 4-ethoxy-1-naphthylamines are likely formed by the rearrangement of the naphthylhydroxylamines, intermediates in the reduction processes. The mechanism for this rearrangement may be similar to that of the acid rearrangement of phenylhydroxylamine[6]. The formation of both 4-ethoxy-1-naphthylamine and 4-ethoxy-2-methyl-1-naphthylamine can be represented by the following scheme:



This reaction mechanism involves 4 equivs. per mole in the reduction of the nitro compound to the amine rather than the usual 6 equivs. per mole. Results calculated on the basis of the weight of copper lost during the reaction were high (4.20 equivs. for 2-methyl-1-nitronaphthalene and 4.73 equivs. for 1-nitronaphthalene) which suggests that other reactions (*e.g.*, direct reduction to the amine) occur simultaneously.

Phenylhydrazines reduce cupric ion to copper metal according to reaction 2 and would be expected to interfere.

$$ArNHNH_2 + 2Cu^{+2} + H_2O = ArOH + 2Cu + N_2 + 4H^+ \quad . \; . \; . \; . \; . \; . \quad (2)$$

A sample of 2,4-dinitrophenylhydrazine was analyzed by the usual technique. Colloidal copper was formed soon after reaction commenced. Attempts to retain all the colloidal copper on a medium porosity sintered-glass crucible were unsuccessful and high results were obtained.

Complexing anions, such as the halides, which stabilize the cuprous state interfere. Several runs were made with equimolar amounts of 2,4-dinitrotoluene and chloride ion. After 1.5 h reflux using Ether 141 as the organic solvent, the maximum result was 45% of theoretical based on two equivs. per mole copper or 90% based on one equiv. per mole of copper. An attempt was made to complex all the copper as the chlorocuprous ion by carrying out the reaction in 6 *N* hydrochloric acid. However, blank determinations run in this media were very large, approaching 0.1 g. It may be shown from the data given by DIEHL[7] that copper in the presence of a concentrated chloride solution is capable of being oxidized by a concentrated acid solution. Therefore blank determinations are large and the results of analysis are highly questionable.

m-Iodonitrobenzene gave results *ca.* 4% high when the reaction was run for 1.5 to 2 h using either Ether 141 or ethanol as solvent. Partial reduction of the iodo group according to reaction 3 was suspected.

$$9Cu + 2IArNO_2 + 16H^+ = 7Cu^{+2} + Cu_2I_2 + 2ArNH_3^+ + 4H_2O \quad . \; . \; . \; . \quad (3)$$

The reduction product after prolonged reaction was identified as follows. *m*-Iodonitrobenzene was refluxed for 8 h in the ethanol-acid solvent. The formation of a white precipitate, presumably cuprous iodide, in the refluxing solution was noted. The benzamide of the resulting amine was prepared by the Schotten-Baumann procedure. The sample was compared with an authentic sample of benzanilide by means of mixed melting point and infrared spectra. The reduction product was benzanilide and resulted from dehalogenation of the benzene ring. A determination of the moles of copper reacted per mole of compound gave the result 4.48 which is in excellent agreement with the value 4.50 predicted from equation 3. Thus the iodine may be quantitatively removed by prolonged reaction, but is only partially reduced during normal reaction periods. Only the nitro group in *m*-chloronitrobenzene is reduced.

Inorganic oxidizing agents which would react with copper metal (*e.g.*, nitrate or ferric ion) would interfere. Aldehydes, ketones, carboxylic acids, alcohols, phenols, amines, and nitriles are among those functional groups which do not interfere with this determination.

SUMMARY

An indirect gravimetric method for the determination of organic nitro, nitroso and azo compounds has been investigated. The amount of nitro, nitroso, and azo compound present is calculated from the loss in weight of copper metal during the reduction of the compound to the amine. Interferences are discussed in detail. No standard solutions are required and only commonly available equipment is used. Accuracy is of the order of ± 0.5%.

RÉSUMÉ

Une méthode gravimétrique indirecte a été examinée pour le dosage des nitro-, nitroso- et azocomposés organiques. Elle est basée sur la diminution de poids du cuivre métallique, utilisé pour la réduction de ces substances en amines.

ZUSAMMENFASSUNG

Beschreibung einer indirekten gravimetrischen Methode zur Bestimmung von organischen Nitro-, Nitroso- und Azoverbindungen. Sie beruht auf der Feststellung des Gewichtsverlustes des zur Reduktion verwendeten metallischen Kupfers.

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AMPEROMETRIC TITRATION OF ALBUMIN IN BLOOD SERUM BY COPPER(II)

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In a recent study in these laboratories, it has been shown that in ammoniacal buffer of pH 9.2, copper(II) reacts with bovine serum albumin in a mole ratio of one to one but does not react with human γ-globulin under similar conditions[1]. Because of the structural similarity of bovine serum albumin to human serum albumin, these results suggest that the reaction of copper(II) with albumin can be made the basis for an amperometric titration of albumin in blood serum with copper(II). This was substantiated by the titration of a sample of fractionated serum which revealed that the only substantial consumption of copper(II) occurred in the albumin fraction.

This paper reports the results of titration of some 50 samples of normal sera and

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17 samples of cancerous sera with copper(II). Facilities for routine electrophoretic analysis of blood sera were not available to us. However, it was possible to obtain independent analyses of the serum samples at the Laboratory of the University of Minnesota Hospital. These analyses were carried out by precipitation in 28% sodium sulfite solution[2,3] which was the method then in routine use in the Hospital laboratory. While this method yields results which are quite useful for routine purposes, it is not as accurate as the electrophoretic procedure, and comparison of the copper(II) titration values with electrophoretically analyzed serum samples would be desirable.

The sulfhydryl content of each sample was also determined amperometrically[4,5]. No simple relation between sulfhydryl and albumin content (from copper titration) was found, and the data are therefore not reported. In agreement with previous work[5] both sulfhydryl and albumin were in general lower in pathologic sera than in normal sera.

EXPERIMENTAL

Materials

Standard copper sulfate solutions were prepared by accurate dilution of a more concentrated solution which had been standardized iodometrically. Conductivity water was used in the preparation of all solutions. Solutions were deaerated with Linde nitrogen of 99.9% purity. All other chemicals used were reagent grade.

Plasma samples

Blood samples were obtained from patients at the University of Minnesota Hospital. The samples were allowed to stand at room temperature until clotting occurred and then centrifuged. The serum was drawn off with a hypodermic syringe and stored in a refrigerator at 4°.[6] Titrations were carried out the same day the samples were drawn.

Titrations

Amperometric titrations were carried out with a circuit similar to that described by LINGANE AND KOLTHOFF[7]. The platinum electrode was rotated at a constant speed of 600 or 900 r.p.m. by a Bodine synchronous motor. Potentials refer to the saturated calomel electrode. The titration vessels were 125-ml beakers fitted with rubber stoppers with holes for the indicator electrode, nitrogen inlet and outlet, salt bridge, and buret. The proper quantity of buffer (usually 25 ml of a solution 0.1 M in ammonia and 0.1 M in ammonium nitrate, pH 9.2) and one ml of blood serum were placed in the titration cell and deaerated with a stream of nitrogen which had been previously passed through buffers of the same composition. Care was taken to avoid any loss of protein through the nitrogen outlet tube because of foaming of the solution after the serum was added. Nitrogen was passed through the solution continuously during the titration. Titrants (10^{-1}–10^{-3} M) were added from a Gilmont ultramicroburet of 0.1-ml total capacity or from a semi-microburet with 0.01 ml divisions.

The titrations were carried out at a potential of −0.4 V *vs.* the saturated calomel electrode. It was found that there was a considerable tendency for the galvanometer to drift to lower values after each addition of the reagent. Accordingly, readings were taken at uniform intervals (usually one min) after each addition of titrant. End-points were found by the usual plot of current *vs.* volume of titrant added. A typical titration is shown in Fig. 1. The end-points were quite reproducible.

A sample of normal serum fractionated by starch block electrophoresis was provided by Dr. H. H. ZINNEMAN of the Minneapolis Veterans' Hospital. Both the whole serum and each individual fraction were titrated with copper(II) under the conditions described previously.

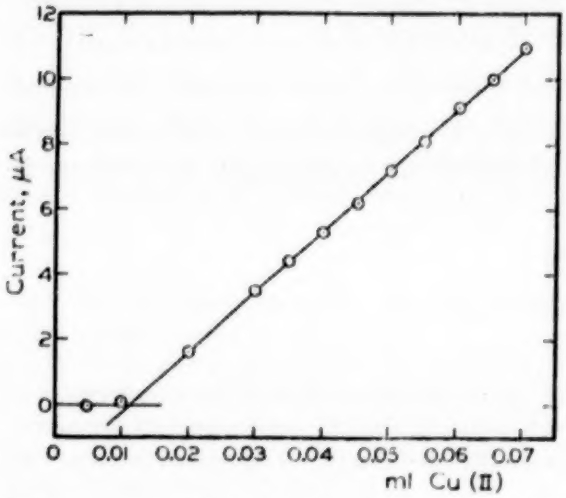

Fig. 1. Titration of blood serum with copper(II). One ml serum in 25 ml buffer, 0.1 M NH_3 + 0.1 M NH_4NO_3, pH 9.2. $CuSO_4$, $4.77 \cdot 10^{-2}$ M, Rotated platinum electrode, 900 r.p.m. —0.4 V *vs.* S. C. E.

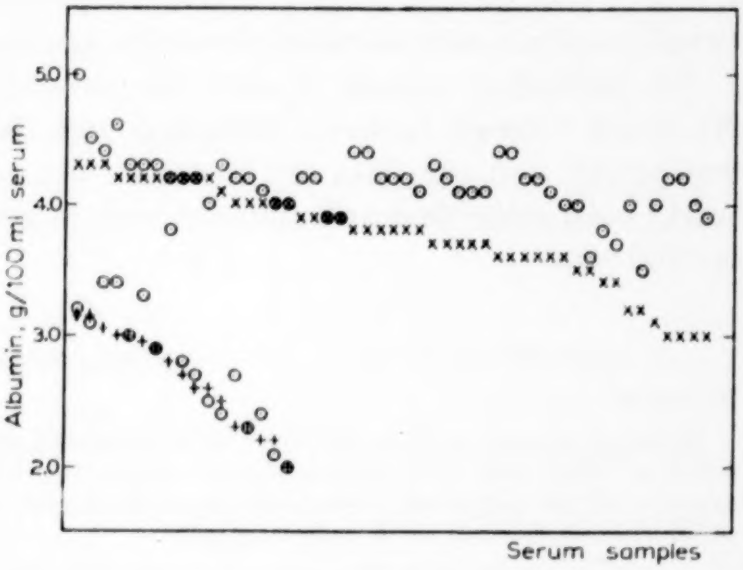

Fig. 2. Albumin content of normal and cancerous blood sera. x = Copper(II) titration values of normal sera. + = Copper(II) titration values of cancerous sera. ⊙ = Neutral salt fractionation values.

RESULTS AND DISCUSSION

The results of this investigation are shown in Fig. 2 which gives a comparison of the albumin values determined amperometrically with those determined by fractional precipitation. It can be seen that there is essential agreement between the methods, particularly for the pathologic sera. In general, the precipitation method tends to yield higher albumin values than the copper titration method, especially for the normal sera. This is attributed to the imperfect separations obtained by the salt fractionation procedure.

TABLE I

TITRATION OF BLOOD SERUM WITH Cu(II)

Medium: 0.1 M NH_3 + 0.1 M NH_4NO_3, pH 9.2; R.p.e. at 600 r.p.m., —0.4 V

Serum fraction	*Cu(II) value, as g % albumin*
Albumin	3.41
α_1-globulin	0.25
α_2-globulin	0
β-globulin	0
γ-globulin	0
Total	3.66
Whole serum, by Cu(II)	3.68
Whole serum, tyrosine	3.70

The results obtained on the sample of fractionated serum are given in Table I. While the unusually close agreement between values is certainly fortuitous, it is significant that over 93% of the copper titer of the whole serum is accounted for in the albumin fraction. The remaining 7% occurs in the α_1-globulin fraction and can be attributed to overlap of the albumin and α_1-globulin fractions. From these experiments it is concluded that under these conditions, the copper titration is specific for albumin.

ACKNOWLEDGEMENT

We wish to express our appreciation to the University of Minnesota Hospital staff for the blood samples and their analysis and to Dr. H. H. ZINNEMAN for the sample of fractionated blood serum. This work was supported by grants from the U.S. Public Health Service and the Louis and Maud Hill Family Foundation.

SUMMARY

Determination of the albumin content of blood serum by amperometric titration with copper(II) in ammoniacal buffer of pH 9.2 yields values in essential agreement with, but in general somewhat lower than, those obtained by precipitation in 28% sodium sulfite solution. While the amperometric titration method gives reproducible results of the right order of magnitude, comparison of results with a large number of electrophoretically analyzed samples would be desirable.

RÉSUMÉ

Les auteurs ont effectué une étude du dosage de l'albumine dans le sérum sanguin, par titrage ampérométrique au moyen de cuivre(II).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Albumin in Blutserum durch amperometrische Titration mit Kupfer(II)-Lösung.

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THE DETERMINATION OF ARSENIC IN TREATED WOOD

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INTRODUCTION

Arsenical mixtures have been used for many years as wood preservatives and more recently in the form of copper chrome arsenates and copper zinc chrome arsenates. The available methods of analysis for arsenic in wood treated with these preservatives have been examined to determine their suitability as rapid routine procedures. Any method adopted should enable the determination of 0.6 mg of arsenic pentoxide with a precision of ± 5% or better without interference from the remaining preservative compounds or phosphorus which is always present in wood frequently in amounts equivalent to the lower limits of arsenic to be determined.

Hitherto, the method which has been used in this laboratory has involved the destruction of the wood substance with mixed nitric, sulphuric and perchloric acids followed by the distillation of the arsenic as As^{+3} from hydrochloric acid using ferrous sulphate as the reducing agent[1]. The distillate was subsequently titrated with standard iodine solution. This method is somewhat tedious on a routine scale though it is known to give good results and our experience showed that one operator could carry out about ten duplicate determinations per day using two sets of distillation equipment. It was therefore hoped that any new method would materially increase the number of analyses per day.

The methods examined may be classified as follows:

I. *Colorimetric.* (a) Arsenomolybdate, (b) molybdenum blue, (c) arseno-vanado-molybdate.

II. *Turbidimetric.* Precipitation of As° by hypophosphorous acid or stannous chloride.

III. *Volumetric.* (a) Reduction to As^{+3} and titration with iodine, chloramine T, bromate or ceric sulphate. (b) Reduction to As° and titration with iodine, bromate or chloramine T.

As it was known[2] that phosphorus interfered in methods I (a) and (b), a study of the ultraviolet spectra of arseno-molybdic and phospho-molybdic acids was made to examine the possibility of a determination in this region. No satisfactory differences appeared in the absorption curves. The extraction procedures, for the removal of molybdophosphoric acid, of FARRER AND NUIR[3] and MERVEL[4] were examined as a means of overcoming the interference from phosphorus. Such procedures were found to offer little advantage in convenience compared with the old method.

The method of GULLSTROM AND MELLON[5] for the determination of arsenic as molybdo-vanado-arsenate was examined in regard to its suitability in the presence of phosphorus which is also known to form a similar heteropoly acid. Unfortunately the method was found to be less sensitive for arsenic and the contaminating phosphorus which would at times be present in excess of the arsenic seriously reduced the suitability of the method.

Turbidimetric methods based on the precipitation of arsenic as As° have been proposed by DELAVILLE AND BELIN[6] and KING AND BROWN[7] but it was found that rapid coagulation of the arsenic occurred which could not be stabilized with gelatine or silicate and the method gave erratic results.

Procedures based on the precipitation of arsenic as As° developed by EVANS[8] were examined but were found to offer no saving in time as compared with the old method. It was however noticed that hypophosphorous acid is oxidized by sulphuric acid when heated to fumes and therefore attempts were made to carry out the determination by adding slight excesses of hypophosphorous acid to the sulphuric acid solution of the arsenate and subsequently heating to fumes. The arsenic initially precipitated as the metal and subsequently redissolved to give As^{+3}. The excess hypophosphorous acid was oxidized during the fuming to dissolve the arsenic and any reduced copper present was also reoxidized to Cu^{+2}. After dilution the arsenic was titrated with ceric sulphate and the procedure gave excellently reproducible results. Unfortunately the recoveries were only of the order of 90% and the method was abandoned. Other reducing agents such as sulphide, thiosulphate and thioacetamide were tried but none of these gave good results although, in the case of the sulphide, the results were again reproducible but low.

FINAL METHOD

The method of SCHULEK AND VILLECZ[9] of reduction to As^{+3} with hydrazine sulphate was tested and found to give excellent results. Some modifications were made to the procedure. Hydrazine sulphate was added as a saturated aqueous solution and titration was with standard ceric sulphate using ferrous *o*-phenanthroline perchlorate as the indicator instead of the bromate procedure. Corrections for blank and any reducing substances present were made by a preliminary titration to the end-point without the addition of the osmic acid catalyst followed by titration of the As^{+3} after addition of the catalyst. The following method based on that of SCHULEK AND VILLECZ[9] for the determination of arsenic in treated wood was adopted.

EXPERIMENTAL

Reagents

Concentrated nitric acid, concentrated sulphuric acid, hydrazine sulphate. Saturated aqueous solution. Ceric sulphate 0.1 *N*, ceric sulphate 0.01 *N*. Osmium tetroxide 0.25% in 0.1 *N* sulphuric acid, ferrous *o*-phenanthroline perchlorate and a saturated aqueous solution.

Procedure

Transfer a weighed 1.000-g portion of treated wood ground to pass a 30-mesh sieve to a 200-ml Kjeldahl flask. Add 25 ml conc. nitric acid and 3 ml conc. sulphuric acid.

Gently heat the contents of the flask until the initial vigorous reaction has subsided and thereafter heat more strongly until strong fumes of sulphuric acid appear. Should the digest show signs of charring – the development of brown colour – several drops of nitric acid will clear the solution. It may be necessary in the case of very resinous samples to add several additional small portions of nitric acid. The final digest should be clear green.

Transfer the digested sample quantitatively to a 150-ml Erlenmeyer flask and heat to fumes of sulphuric acid again.

Cool, add 1 ml of hydrazine sulphate solution, rinsing the neck of the flask with distilled water to wash all traces of hydrazine sulphate into the acid mixture. Heat to fumes once more and fume for ten min. Cool and dilute with 40 ml of distilled water.

Add 0.5 ml of ferrous *o*-phenanthroline perchlorate indicator and titrate with standard ceric sulphate, approximately 0.01 *N* (prepared by dilution of the stock solution of 0.1 *N* reagent), using a 2-ml microburette. The titrant should be added in 0.01-ml portions and generally about 0.07 ml will be required for the titration (equivalent to about 0.004% As_2O_5). At the end-point the colour changes from orange-red to a faint green. The volume taken need not be recorded but the end-point should be stable for 15 sec. Read the burette and add 3 drops of osmium tetroxide catalyst when the colour of the reduced form of the indicator is restored and titrate with the standard ceric sulphate adding the titrant slowly as the end-point is approached.

Standardize the approximately *N*/100 ceric sulphate by titrating aliquots of standard *N*/100 arsenate solution carried through the above process or alternatively *N*/100 arsenite solution.

Notes on the method

(1) In instructions for the digestion of organic material as a preliminary to the determination of arsenic, it is often stated that charring should be avoided as this will tend to cause reduction and volatilization of the arsenic. Since any charring with the above method can occur only after boiling off of the nitric acid when all chlorides should have been volatilized and, as it is implicit in the hydrazine sulphate reduction that As^{+3} is non volatile at the temperature at which sulphuric acid fumes, it did appear that there was not much likelihood of serious loss of arsenic should slight charring occur during digestion. A test showed that after one hour's charring losses of arsenic did occur but these were not unduly high when the time of charring was taken into consideration (see Table I). Thus one can reasonably confidently assume that the occasional slight charring which occurs, if it is not unduly prolonged, is not a serious hazard in the analytical process.

TABLE I

EFFECT OF CHARRING ON As_2O_5 RECOVERIES

Not charred *mg* As_2O_5	*Charred 1 h* *mg* As_2O_5
0.58	0.54
0.59	0.54
1.18	1.13
1.17	1.13
2.41	2.36
2.41	2.34

(2) The fuming after transference to the Erlenmeyer flask is to remove the final traces of nitric acid. Should brown fumes develop on fuming then an additional dilution and fuming should be made as excess nitric acid is still present.

(3) The quantity of hydrazine sulphate solution is adequate for at least 14 mg As_2O_5.

(4) Dilute *N*/100 ceric sulphate solutions require some days standing in order to stabilize by oxidation any reducing substances in the solution and should therefore be standardized daily until the titre becomes constant.

(5) If the sample has been insufficiently fumed to destroy the excess hydrazine sulphate difficulty will be experienced in obtaining a stable end-point in the initial titration. In this case it is preferable to begin the determination again.

RESULTS

The results obtained by the method are given in Tables II and III.

Ceric sulphate standardized by 10 replicate titrations of *N*/100 arsenite at the 2.87-mg level.

DISCUSSION OF RESULTS

The results in Table II show good recoveries of added arsenic and the observation of SCHULEK AND VILLECZ[9] that low recoveries are obtained in the presence of copper is not supported. The results in Table III show excellent agreement between the old and new methods and this is especially interesting as determinations were carried out on separately weighed wood samples.

The new method represents a considerable saving in time allowing the determination of some forty samples per day as against ten per day by the old method with two distillation units in operation. The main limiting factor with the method is now the number of samples which can be digested per day.

TABLE II

TITRATIONS USING ARSENIC PENTOXIDE SOLUTIONS

10 replicates at each level

Taken *mg* As_2O_5	*Found*[a] *mg* As_2O_5	*Found*[b] *mg* As_2O_5
2.87	Max. 2.91	2.89
	Min. 2.88	2.85
	Mean 2.90	2.87
0.58	Max. 0.60	0.60
	Min. 0.58	0.56
	Mean 0.59	0.58

[a] Arsenic pentoxide alone.

[b] Arsenic pentoxide + 0.01 g $CuSO_4 \cdot 5H_2O$ + 0.01 g $K_2Cr_2O_7$. (To simulate working conditions)

TABLE III

COMPARISON OF RESULTS OBTAINED BY DISTILLATION AND THE HYDRAZINE SULPHATE PROCEDURES[a]

Results as % As_2O_5

Sample No.	*By distillation*	*By hydrazine sulphate*
1	0.016	0.016
2	0.026	0.027
3	0.046	0.046
4	0.051	0.047
5	0.062	0.062
6	0.071	0.069
7	0.078	0.077
8	0.128	0.127
9	0.235	0.215
10	0.274	0.265

[a] Wood samples treated with copper chrome arsenate.

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SUMMARY

The Schulek and von Villecz method for the determination of arsenic in organic compounds has been applied to the determination of arsenic in wood. Copper and chromium do not interfere.

RÉSUMÉ

La méthode de Schulek et de von Villecz pour le dosage de l'arsenic dans les composés organiques a été appliquée au dosage de l'arsenic dans des bois traités.

ZUSAMMENFASSUNG

Es wird die Anwendung der Methode zur Bestimmung von Arsen in organischen Substanzen nach Schulek und Villecz auf die Bestimmung von Arsen in Holz beschrieben.

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Short Communication

Thermographic semiquantitative micro-determination of sulfuric acid

When concentrated sulfuric acid is placed in contact with filter paper, it readily chars the cellulose fibers of the paper. But with dilute aqueous solutions of sulfuric acid, the paper remains white. However, if the paper impregnated with sulfuric acid solutions is heated at 170° for 10 min, yellow, brown or black spots appear, the color depending on the acid concentration. This is the basis of a new technique, *thermography*, where the color development is due to heating and is made without reagents. Perchloric and phosphoric acids react similarly, and can also be determined.

Whatman No. 1 filter paper can be used for the semiquantitative determination of sulfuric acid in aqueous solutions. The following scales are used:
a) 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0 and 100.0 μg of sulfuric acid per 2 μl. b) 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0 μg of sulfuric acid per 10 μl.

The comparison of colors obtained with unknown solutions with that of the scales showed good reproducibility. The color of the spots is permanent and the papers can be stored.

The determination of sulfate in waters after conversion to sulfuric acid with the aid of cation-exchangers is being studied.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

IV[1]. A METHOD OF CALCULATING ASYMMETRICAL TITRATION CURVES AVOIDING THE USE OF CUBIC EQUATIONS

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Many ion combination reactions in analytical use result in the formation of unsymmetrical reaction products, such as,

$$2B^+ + A^{-2} \rightleftarrows B_2A$$
$$B^{+2} + 2A^- \rightleftarrows BA_2$$

The product may be a sparingly soluble salt, such as silver oxalate or calcium fluoride, or it may be a sparingly ionised solute, either a simple molecule such as mercuric bromide in mercurimetry, or a complex molecule or ion such as the dicyanoargentate ion in argentimetry. Calculation of titration curves for such reactions involves in the region of the equivalence point the solution of cubic equations. This tedious procedure remains necessary when a specific point fails to be calculated, but may be avoided when constructing curves by the simple device of inverting the equations, so producing quadratic, or even linear equations.

Calculation of ion concentrations

Taking the species BA_2 as an example, and ignoring ion charges, at equilibrium,

$$\frac{[B]\,[A]^2}{[BA_2]} = K \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where K is the ionisation constant of the covalent solute, the instability (dissociation) constant of the complex or the dissolution constant of the precipitate. At points far removed from the equivalence point, the excess of B or A is sufficient to suppress the ionisation of BA_2 to such a level that the error incurred in ignoring this ionisation is negligible, and the ion concentrations can be calculated with adequate accuracy from (2) and (3),

$$[B] = \frac{K[BA_2]}{[A]^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$[A] = \left(\frac{K[BA_2]}{[B]}\right)^{\frac{1}{2}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Approaching or leaving the equivalence point this assumption becomes invalid, and account must be taken of the dissociation of BA_2. Since BA_2 is asymmetrical, different equations are required according to whether B or A is in excess.

1. *B in excess.* If B is in excess to an amount b calculated from the concentration of the reagent and the volume of the titration solution, and the amount of BA_2 is similarly calculated to be c, then the concentrations of the various species have to be calculated from[2]

$$[\mathrm{B}] = b + {}^1\!/_2[\mathrm{A}] \qquad (4)$$

$$[\mathrm{BA_2}] = c - {}^1\!/_2[\mathrm{A}] \qquad (5)$$

$$[\mathrm{A}]^3 + 2\,b[\mathrm{A}]^2 + \mathrm{K}[\mathrm{A}] - 2\,c\mathrm{K} = 0. \qquad (6)$$

The point at which it becomes necessary to change over from the simple equations (2) and (3) to the more precise equations (4–6) is defined by the discriminant[3] (7) for a given maximum permissible relative error E,

$$b \leqslant \left\{\left(\frac{1-E}{2E}\right)^2 Kc\right\}^{\frac{1}{2}} \qquad (7)$$

2. *A in excess.* If the excess of A is calculated to be a, then the following equations apply[2]

$$[\mathrm{A}] = a + 2[\mathrm{B}] \qquad (8)$$

$$[\mathrm{BA_2}] = c - 2[\mathrm{B}] \qquad (9)$$

$$4\,[\mathrm{B}]^3 + 4\,a[\mathrm{B}]^2 + (a^2 + K)[\mathrm{B}] - \mathrm{K}c = 0 \qquad (10)$$

and are required to avoid a relative error greater than E according to the discriminant[3] (11) when

$$a \leqslant \left(2\,\frac{(1-E)}{E}\,Kc\right)^{\frac{1}{2}} \qquad (11)$$

Calculation of titration curves

1. *Standard method.* By solution of the discriminants (7) and (11) for a predetermined permissible relative error, or by other means, the region on either side of equivalence within which the exact equations are required is defined. For selected increments of titrant, a or b, as appropriate is calculated, and the ion concentrations calculated from (2) and (3) outside or (4–10) inside the range defined by the discriminants. At the equivalence point, ion concentrations are calculated directly from (1)[2].

Unless the constant K has a very small value, less than 10^{-15}, the region requiring use of the exact cubic equations extends for a considerable distance on either side of the equivalence point. To avoid this tedious solution of cubics, the calculation may be reversed; instead of calculating from the volume axis to the pM axis, that is, supplying values for titrant increments and calculating ion concentrations, values may be placed on the ion concentration and the titrant volume calculated therefrom.

This may be effected by rearranging equations (6) and (10) in terms of b and a thus,

$$b = {}^1\!/_2\left\{\frac{K}{[\mathrm{A}]}\left(2\,\frac{c}{[\mathrm{A}]} - 1\right) - [\mathrm{A}]\right\} \qquad (12)$$

$$a^2 + 4[\mathrm{B}]a + 4[\mathrm{B}]^2 + K\left(\frac{[\mathrm{B}] - c}{[\mathrm{B}]}\right) = 0 \qquad (13)$$

whence

$$a = \left\{\frac{K}{[\mathrm{B}]}\,(c - [\mathrm{B}])\right\}^{\frac{1}{2}} - 2[\mathrm{B}] \qquad (13a)$$

2. *Simplified method.* Solution of the discriminants again defines the region wherein exact equations are required. Outside this region, the normal process is followed. Inside this region, the steps are as shown.

a. Place a value on [B] or [A] as appropriate.
b. Calculate a or b from (13a) or (12).
c. Calculate the true value of [A] or [B] from (8) or (4).
d. Calculate the corresponding volume of titrant (or percentage of reaction).

Calculation of titrant volume from concentrations

Step d and the corresponding conversion of the solution of the discriminant to titrant volume, may call for calculation to a high degree of precision to obtain significant results if the total titrant volume is used. It is better, therefore, to calculate v_1, the difference from 100% reaction. If V% of titrant has been added, then $V = 100 - v_1$. In a 100-ml titration, V and v_1 give the volume directly in ml, and for any other titration volume, say x, the volume in ml will be given by $V \times x/100$ and $v_1 \times x/100$. If the molarities of the two solutions are M_A and M_B, then, before the equivalence point with B as titrant,

$$v_1 = \frac{200a}{(M_A + a)} \qquad (14)$$

With A as titrant,

$$v_1 = \frac{200b}{(M_B + b)} \qquad (15)$$

After the equivalence point, at a point v_2% past the equivalence point, $V = 100 + v_2$, and with B as titrant,

$$v_2 = \frac{200b}{(M_B - b)} \qquad (16)$$

With A as titrant,

$$v_2 = \frac{200a}{(M_A - a)} \qquad (17)$$

Mercuric chloride may be used as an example with a very low dissociation constant, $6 \cdot 10^{-14}$, in illustration of the method. In the titration of 100 ml of 0.1 M chloride solution with 0.05 M mercuric perchlorate, *at the equivalence point* $c = 2.5 \cdot 10^{-2}$ and, from (1), $[Hg^{+2}] = 7.21 \cdot 10^{-6}$ and $[Cl^-] = 1.442 \cdot 10^{-5}$.

Before the equivalence point, allowing a maximum relative error of 1% ($E = 0.01$), solution of the discriminant (11) and conversion of the value of a so found into terms of volume by (14) shows that the simple equation (3) is valid up to 0.06 ml before the equivalence point, and from (2) the mercuric ion concentration at this point is $1.56 \cdot 10^{-6}$. From this point the steps are:

a. set $[Hg^{+2}]$ at values between $1.56 \cdot 10^{-6}$ and $7.21 \cdot 10^{-6}$, say $2 \cdot 10^{-6}$,
b. calculate a from (13a) which gives the value $2.34 \cdot 10^{-5}$,
c. should a pCl curve be required, calculate $[Cl^-]$ from (8), giving $2.74 \cdot 10^{-5}$,
d. calculate v_1 from (14), giving 0.047 ml, so that the titrant volume $V = 99.953$ ml.

After the equivalence point, the discriminant (7) gives a value of b of $1.545 \cdot 10^{-5}$, which from (16) indicates that exact equations are required until 0.62 ml of titrant has been added in excess. This point corresponds, from (3), to a chloride ion concentration of $9.85 \cdot 10^{-6}$.

a. Set $[Cl^-]$ at values between $9.85 \cdot 10^{-6}$ and $1.442 \cdot 10^{-5}$, say $1.0 \cdot 10^{-5}$,
b. Calculate b from (12), giving the value $1.0 \cdot 10^{-5}$,
c. Calculate $[Hg^{+2}]$ from (4), giving the value $1.5 \cdot 10^{-5}$,

d. Calculate v_2 from (16), giving the value 0.04 ml, so that the titrant volume $V = 100.04$ ml.

Precipitimetric titrations

The procedure and equations given apply strictly to all reactions resulting in the formation of species BA_2 or B_2A, but in the special case of sparingly soluble substances, it is customary to deal in terms of the ion product (solubility product S_{B_2A}) instead of the equilibrium constant. Thus the term $c = [B_2A]$ is absorbed into the constant and some simplification of the equations results. Taking the case of the salt B_2A in illustration, the equilibrium constant becomes

$$[B]^2[A] = S_{B_2A}. \qquad (18)$$

Remote from the equivalence point, ion concentrations are calculated from

$$[B] = \left(\frac{S_{B_2A}}{[A]}\right)^{\frac{1}{2}} \qquad (19)$$

$$[A] = \frac{S_{B_2A}}{[B]^2} \qquad (20)$$

If the relative error allowed is E, then if *B is in excess*, when b falls below the value given by the discriminant (21),

$$b \leqslant \left(2\,\frac{(1-E)}{E}\,S_{B_2A}\right)^{\frac{1}{3}} \qquad (21)$$

the following equations are applicable,

$$[B] = b + 2[A] \qquad (22)$$

$$4[A]^3 + 4b[A]^2 + b^2[A] - S_{B_2A} = 0 \qquad (23)$$

Rearrangement of (23) in terms of b gives,

$$b = \left(\frac{S_{B_2A}}{[A]}\right)^{\frac{1}{2}} - 2[A] \qquad (24)$$

which may be used in the simplified procedure.

When *A is in excess*, these equations become,

$$a \leqslant \left\{\left(\frac{1-2E}{2E}\right)^2 S_{B_2A}\right\}^{\frac{1}{3}} \qquad (25)$$

$$[A] = a + {}^1\!/_2\,[B] \qquad (26)$$

$$[B]^3 + 2\,a[B]^2 - 2\,S_{B_2A} = 0 \qquad (27)$$

Rearrangement of (27) gives

$$a = \frac{S_{B_2A}}{[B]^2} - \frac{[B]}{2} \qquad (28)$$

for use in the simplified procedure. Titrant volumes before the equivalence point are calculated from (14) and (15), and after the equivalence point from (16) and (17).

For example, the following data were calculated by this method for drawing pAg and pC_2O_4 curves for the titration of 100 ml of 0.05 *M* oxalate with 0.1 *M* silver nitrate, using the value $1.1 \cdot 10^{-11}$ for the solubility product, and allowing an error of 1% ($E = 0.01$).

AT THE EQUIVALENCE POINT

$[Ag^+] = 2.8 \cdot 10^{-4}$; pAg = 3.553; $[C_2O_4^{-2}] = 1.4 \cdot 10^{-4}$; $pC_2O_4 = 3.854$.

BEFORE THE EQUIVALENCE POINT

$[Ag^+]$	pAg	a	$[C_2O_4^{-2}]$	pC_2O_4	*Volume of titrant added, ml*
$1.0 \cdot 10^{-4}$	4.0	$1.05 \cdot 10^{-3}$	$1.10 \cdot 10^{-3}$	2.958	95.89
$1.4 \cdot 10^{-4}$	3.854	$4.91 \cdot 10^{-4}$	$5.61 \cdot 10^{-4}$	3.251	98.065
$1.6 \cdot 10^{-4}$	3.796	$3.495 \cdot 10^{-4}$	$4.295 \cdot 10^{-4}$	3.367	98.612
$1.8 \cdot 10^{-4}$	3.745	$2.598 \cdot 10^{-4}$	$3.398 \cdot 10^{-4}$	3.469	99.008
$2.0 \cdot 10^{-4}$	3.699	$1.75 \cdot 10^{-4}$	$2.75 \cdot 10^{-4}$	3.561	99.303
$2.3 \cdot 10^{-4}$	3.638	$8.28 \cdot 10^{-5}$	$2.078 \cdot 10^{-4}$	3.682	99.629
$2.5 \cdot 10^{-4}$	3.602	$5.10 \cdot 10^{-5}$	$1.76 \cdot 10^{-4}$	3.754	99.796
$2.6 \cdot 10^{-4}$	3.585	$3.26 \cdot 10^{-5}$	$1.626 \cdot 10^{-4}$	3.789	99.87

AFTER THE EQUIVALENCE POINT

$[C_2O_4^{-2}]$	pC_2O_4	b	$[Ag^+]$	pAg	*Volume of titrant added, ml*
$1.2 \cdot 10^{-4}$	3.921	$6.275 \cdot 10^{-5}$	$3.028 \cdot 10^{-4}$	3.519	100.126
$1.0 \cdot 10^{-4}$	4.000	$1.315 \cdot 10^{-4}$	$3.315 \cdot 10^{-4}$	3.48	100.263
$8.0 \cdot 10^{-5}$	4.097	$2.105 \cdot 10^{-4}$	$3.705 \cdot 10^{-4}$	3.431	100.422
$5.0 \cdot 10^{-5}$	4.301	$3.69 \cdot 10^{-4}$	$4.690 \cdot 10^{-4}$	3.329	100.74
$3.0 \cdot 10^{-5}$	4.523	$5.455 \cdot 10^{-4}$	$6.055 \cdot 10^{-4}$	3.218	101.098
$1.0 \cdot 10^{-5}$	5.000	$1.028 \cdot 10^{-3}$	$1.048 \cdot 10^{-3}$	2.979	102.075
$5.0 \cdot 10^{-6}$	5.301	$1.473 \cdot 10^{-3}$	$1.483 \cdot 10^{-3}$	2.829	102.985

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SUMMARY

A method is offered for the exact calculation of data for unsymmetrical titration curves in which the solution of cubic equations is avoided. Instead of calculating ion concentrations from the volume of titrant added in the conventional way, the calculation is reversed, and titrant volumes are calculated from supplied values of the concentration of the ion which is not in excess. The necessary precision is attained more easily by calculating the difference between the titrant volume and the equivalence point volume, so that the use of seven figure logarithms is unnecessary.

RÉSUMÉ

Une méthode est proposée pour le calcul précis dans le cas des courbes asymétriques de titrage; on évite ainsi l'emploi d'équations du troisième degré. Contrairement à la méthode habituelle, on ne calcule pas les concentrations des ions à partir du volume de la solution étalon ajoutée, mais le volume de cette dernière est calculé par la concentration de l'ion qui n'est pas en excès.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur genauen Berechnung der Daten für unsymmetrische Titrationskurven unter Vermeidung kubischer Gleichungen. Im Gegensatz zu dem üblichen Verfahren wird das Volumen der Titierflüssigkeit aus gegebenen Werten der Konzentration des nicht im Ueberschuss vorhandenen Ions berechnet.

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ANALYSIS OF PEROXIDES

SEPARATION AND IDENTIFICATION BY PAPER CHROMATOGRAPHY

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INTRODUCTION

The analysis of peroxides, and especially the separation and identification of the various components of mixtures of peroxides formed during the combustion of hydrocarbons in the gas-phase, has proved to be of considerable difficulty. Volumetric methods, such as the release of iodine from acidified potassium iodide or the oxidation of stannous chloride in alkaline solution, or colorimetric methods using titanous sulphate or ferrous thiocyanate are really only suitable if a single peroxide or a simple mixture of known components is to be analysed. HOLMAN *et al.*[1] have claimed that in the near infra-red there are characteristic peaks which may be used for the identification and determination of individual hydroperoxides, but even so analysis of other than simple mixtures would be difficult. The polarography of peroxides has been investigated by a number of workers[2-4], but the method appears to be best suited to the estimation of hydrogen peroxide in the presence of other peroxides, the polarograms of which are very similar.

During the last few years it has become apparent that chromatography is a powerful tool for peroxide analysis. Vapour-phase chromatography can only be used for the more volatile compounds[5], since otherwise the column temperature has to be so high that decomposition may occur. Paper chromatography, however, offers greater possibilities. TAYLOR[6] has shown that hydrogen peroxide, for instance, is separated from other peroxides on untreated paper, whilst other workers[5,7,8] using various moving and stationary phases have found that a number of peroxides have characteristic R_F values. Nevertheless the methods used have some disadvantages. The more volatile compounds, which are often of interest to the combustion chemist, tend to be lost by evaporation from the paper, and alkyl hydroperoxides are not separated one from another. Also the method for the detection of the spots is not always satisfactory. It was therefore decided to investigate the paper chromatography of peroxides in more detail, since the apparatus is simple and only small amounts of material are needed. The work has shown that the various classes of peroxide (*e.g.* hydrogen peroxide, hydroperoxides, peracids, dialkylperoxides) may be simply distinguished, and that the members of each class may be identified in most cases.

EXPERIMENTAL

The apparatus was of conventional design. A large glass tank, which could be made airtight at the top by a glass plate and rubber seal, contained the trough for the moving phase. This was also present in a beaker so that the atmosphere was saturated during a run. The paper, Whatman No. 3, was clamped by large spring clips between two glass plates to prevent evaporation of any volatile components[9]. The plates were wide enough so that the clips did not overlap the paper, since if they did the outer spots drifted towards the edge. The length of paper between the solvent surface and the top of the plates was at least 5 cm, since otherwise the solvent front moved too fast and the spots were ill-defined. The paper was either (a) untreated, (b) treated with a 5 or 20-vol % solution of silicone oil in 80–100° petroleum ether and dried in an oven at 110° for 1 h, or (c) treated with a solution of ethylene glycol in acetone (5 or 20% by vol) and dried in a stream of air. With the treated paper it was necessary to cover the glass plates with silicone solution and allow the petroleum ether to evaporate before use, since this made them solvent repellent. With uncoated plates proper chromatograms were unobtainable. Various liquid mixtures were used as the moving phase (see next section). The samples were transferred to the paper by means of a loop of platinum wire, which was heated in a flame just before use to eliminate contamination.

When the solvent front had moved a suitable distance, the paper was removed from between the plates, and the position of the front marked. The chromatogram was dried in a stream of air for as short a time as possible (usually 1–2 min), and immediately sprayed with developer. This was either (a) a solution of ferrous thiocyanate[5], (b) a solution of *p*-phenylenediamine and acetaldehyde in aqueous acetic acid, (c) a dilute solution of *o*-tolidine and a small amount of ferrous ammonium sulphate in aqueous acetic acid, or (d) a 10-vol % solution of hydrogen iodide in glacial acetic acid. With the *o*-tolidine developer the chromatogram was enclosed between plates immediately after spraying to minimize oxidation of the ferrous salt. Characteristic derivatives of hydroperoxides were prepared by adding a sample to a solution of 0.2 g xanthydrol in 2 ml glacial acetic acid.

Concentrated solutions of hydrogen peroxide (97 and 99%), and pure specimens (98%) of *tert.*-butylhydroperoxide, di-*tert.*-butylperoxide and *tert.*-butylperbenzoate were donated by Laporte Chemicals, and *n*-, *sec.*- and *iso*butylhydroperoxides, 3-methylhexane-3-hydroperoxide, 3-methylhexyl-3-peroxytriphenylmethyl and *tert.*-amyl-9-xanthenyl were a gift from DR. A. G. DAVIES (University College, London). Di-*n*-heptylperoxide and *n*-heptyl hydroperoxide were prepared by the method of WILLIAMS AND MOSHER[10], and the other peroxides by the action of hydrogen peroxide on the appropriate alcohols and carboxylic acids or by the reaction of the appropriate aldehydes with hydroperoxides or hydrogen peroxide. The xanthydrol was from Kodak, and all other chemicals were of AnalaR quality.

RESULTS AND DISCUSSION

With the ferrous thiocyanate developer the presence of hydrogen peroxide, hydroperoxides or peracids was shown by red spots which "flashed up" immediately, whereas those due to other peroxides formed more slowly. With the diamine–aldehyde mixture the spots were pale red. The *o*-tolidine gave a blue-green colour only with compounds containing the –OOH group (or with substances which hydrolyze very readily in acid to give this group). With the hydrogen iodide solution nearly all peroxides gave a black or brown spot on a light brown background. The sensitivity of developers decreased in the above order. Two very stable peroxides, di-*tert.*-butylperoxide and 3-methylhexyl-3-peroxytriphenylmethyl, could not be detected on a chromatogram satisfactorily by any method.

A few results using untreated paper and different moving phases are shown in

TABLE I

UNTREATED PAPER

Section (a). Moving phase water–ether–*n*-butanol (1 : 10 : 10 by vol). Rate of movement of solvent front ≈ 4 cm/h.[6]

Section (b). Moving phase, ether. Rate of movement of solvent front ≈ 40 cm/h.

Compound	R_F	*Compound*	R_F
hydrogen peroxide	0.50	hydrogen peroxide	0.14
hydroxyperoxides	0.95–0.98	hydroperoxides	1.0
hydroperoxides	1.0		

Table I. The alkyl hydroperoxides spread across the solvent front in a characteristic way. The limit of detection, *i.e.* the approximate minimum amount which, when transferred to the paper, gave a definite spot on the chromatogram on spraying with the most sensitive developer which reacted with the compound, was 20 μg for hydrogen peroxide.

Table II shows the results using the silicone treated paper. In section (a) the R_F values for various peroxides of relatively low molecular weight are given, whilst in section (b) the values are for the peroxides formed when some hydroperoxides reacted with xanthydrol.

TABLE II

SILICONE TREATED PAPER

Section (a). Stationary phase, silicone from a 5% solution. Moving phase, water–ethanol–chloroform (20 : 17 : 2 by vol). Rate of movement of solvent front ≈ 1.8 cm/h.[5]

Compound	R_F
di-*n*-heptylperoxide	0.018
$(Me_3COO)_2CHMe$	0.49
hydrogen peroxide	0.68
tert.-butyl, 2-hydroxyethylperoxide	0.80
cumene hydroperoxide	0.82
di-2-hydroxyethylperoxide	0.88
alkyl hydroperoxides	1.0

Section (b). Stationary phase, silicone from a 20% solution. Moving phase, 80 vol % methanol in water. Rate of movement of solvent front ≈ 5 cm/h.

Compound mixed with xanthydrol	R_F
tert.-butyl hydroperoxide	0.27, 0.45
tert.-amyl hydroperoxide	0.18, 0.43
n-heptyl hydroperoxide	0.0, 0.09(a), 0.19, 0.30, 0.49(b), 0.67, 0.80. Spots a and b are the strongest

The limits of detection using the silicone treated paper can only be roughly estimated. The value for hydrogen peroxide was again 20 μg, and the limits for the other peroxides must be considerably greater.

The results recorded in Section (b) varied somewhat with conditions, for instance the distance of travel of the moving phase. The *n*-heptyl hydroperoxide contained only a very small of peroxidic impurity, and it is difficult to understand why so many different peroxides were produced. There were always two main spots, a and b, and the maximum number on any chromatogram was six, the average being four. The results, however, from any one mixture of xanthydrol and heptyl hydroperoxide were reproducible. The use of the *o*-tolidine developer showed that no xanthenyl contained an –OOH group. In fact it was necessary to use the hydrogen iodide solution to detect the spots.

The results using the glycol treated paper are recorded in Table III.

It has been found that, using paper treated with a 25% glycol solution and the 5% ether solution as the moving phase, the faster moving peroxides gave more sharply defined spots, though the R_F values were not appreciably different from those in the

TABLE III

GLYCOL TREATED PAPER

Rate of movement of solvent front ≈ 15 cm/h.

Conditions: I. Stationary phase (S), glycol from a 5% solution; moving phase (M), 10 vol % *n*-butanol in 80–100° petroleum ether. II. S, glycol from a 20% solution; M, 50/50 chloroform in 80–100° petroleum ether. III. S, as for II; M, 5 vol % ether in 80–100° petroleum ether.

Compound	R_F		
	I	*II*	*III*
hydrogen peroxide	0.05	0	0
methyl hydroperoxide	0.36	0	0
ethyl hydroperoxide	0.38	0	0
tert.-butyl hydroperoxide	spreads across front	0.35	0.22
n-, *iso*-, *sec.*-butyl hydroperoxide	—	—	0.31
tert.-amyl hydroperoxide	—	—	0.43
n-heptyl hydroperoxide, 3-methylhexyl-3-hydroperoxide	—	—	0.80
cyclohexane hydroperoxide	—	—	0.30
cyclohexene hydroperoxide	—	—	0.14
n-heptan-3,3′-dihydroperoxide[a]	—	—	0.07
2,5-dimethylhexane-2,5-dihydroperoxide	—	—	0.20
cumene hydroperoxide	—	—	0.53
peracetic acid	0.26	0.05	0
perpropionic acid	0.54	0.16	0.11
per-*n*-, per-isobutyric acid	—	0.37	0.30
per-*n*-valeric acid	—	0.57	0.50
per-*n*-hexoic acid	—	0.71	—
percrotonic acid[b]	—	0.23	—
diacetylperoxide	0.37	0.18	—
hydroxymethylhydroperoxide	0.09	0	0
2-hydroxyethylhydroperoxide	0.22	0	0
dihydroxymethylperoxide	0.25	—	—
tert.-butyl, 2-hydroxyethylperoxide	—	—	0.55
n-heptyl, 2-hydroxyethylperoxide	—	—	0.92
cumyl,2-hydroxy-2-phenylethylperoxide	—	—	0.76
tert.-butylperbenzoate	—	—	1.0
di-*n*-heptylperoxide	—	—	0.95
$(Me_3COO)_2CHMe$	—	—	0.95

[a] From the reaction of heptan-3-one and hydrogen peroxide[8].

[b] Actually the main product of the gas-phase oxidation of crotonaldehyde at 150°.

final of column of Table III. The limits of detection for hydrogen peroxide, *tert.*-butyl hydroperoxide and *n*-heptyl hydroperoxide were 0.4, 10 and 20 μg respectively, and the values for the other peroxides will be of the same order.

The resolution possible with the methods described tended to vary with R_F value, since the more slowly moving spots were naturally the more sharply defined. Normally it was possible to separate compounds with low R_F values if these differed by not less than 0.03, and compounds with high R_F values if the difference was greater than 0.06. In general the R_F values were reproducible to within 5–10%.

These results amend and greatly amplify a brief preliminary report of this work[11]. Although the methods have been developed to separate and identify mainly relatively simple aliphatic peroxides, it should be easy to use them for other peroxides. The best method of tackling an unknown mixture will obviously depend on the components which may be expected to be present. However, it is recommended that the untreated paper is first used to detect any appreciable quantity of free hydrogen peroxide, and then as far as possible the glycol treated paper, since with this the chromatograms are obtained relatively quickly (1–2 h). Also the limits of detection are much smaller. In fact if too much peroxide was applied to the paper, smears rather than distinct spots were obtained. The silicone treated paper is best, however, for the identification of the more non-polar peroxides, *e.g.* dialkylperoxides. In fact the conditions given in Table II, Section b, may lead to better resolution in some cases. A check on any hydroperoxides present may be made by means of their xanthydrol derivatives. Also many hydroxyalkylperoxides may be split into their component hydroperoxides and carbonyl compounds by hydrolysis with dilute sulphuric acid. The former can then be identified as described, and the latter by paper chromatography of the dinitrophenylhydrazones[12]. Finally it should be mentioned that a number of synthetic and unknown mixtures have been successfully analysed using the techniques described.

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SUMMARY

The paper chromatography of hydrogen peroxide and numerous organic peroxides (mainly aliphatic) has been investigated under various conditions. By the use of several stationary and moving phases nearly the peroxides may be separated and identified in very small amounts.

RÉSUMÉ

Les auteurs ont effectué une étude par chromatographie sur papier, en vue de l'identification et de la séparation du peroxyde d'hydrogène et de divers peroxydes organiques.

ZUSAMMENFASSUNG

Es wird eine papierchromatische Methode zum Nachweis und zur Trennung von Wasserstoffperoxyd und organischen Peroxyden beschrieben.

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THE COLORIMETRIC DETERMINATION OF ORTHOPHOSPHATE IN THE PRESENCE OF CONDENSED PHOSPHATES

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During studies on the degradative changes in synthetic polymetaphosphates by ultrasonic irradiation[1], it was necessary to estimate the small amounts of orthophosphate originally present and also any orthophosphate found during the exposure. Colorimetric methods where high concentrations of sulfuric acid and molybdate are used[2,3] were inapplicable because of the labile nature of metaphosphate. The method of LOWRY AND LOPEZ[4], which is widely employed to estimate orthophosphate in the presence of acid-labile phosphate esters, was then tried. There was no color formation when fresh solutions of polymetaphosphates were tested, but after subjecting to ultrasonic vibration at 25 kc/sec for 30–60 min in a stainless steel vessel, there was a significant color development when the solutions were reanalyzed. It was found that the color formation due to orthophosphate was suppressed by high concentrations of polymetaphosphate. This inhibition was overcome partially, or nearly completely, by the addition of certain metal ions. The isobutanol extraction method of BERENBLUM AND CHAIN[5], in contrast to the direct colorimetric method of LOWRY-LOPEZ, was found to be suitable for the accurate assay of the orthophosphate in the presence of a large excess of condensed phosphates. With this method the orthophosphate content of the exposed solution was practically the same as that of the unexposed solution.

A study has been made of the influence of various condensed phosphates on the estimation of orthophosphate by the LOWRY-LOPEZ method, and of the addition of microquantities of copper and other metallic ions in preventing the inhibition.

MATERIALS AND METHODS

The technique of irradiation of the condensed phosphates used in these experiments has been reported[1]. The LOWRY-LOPEZ estimation was carried out as described by DAVISON-REYNOLD, BARRUETO AND LEMON[6]. Acidic deproteinizing agents were not present and hence sodium acetate was not added to neutralize free acid. The system contained 2 ml of the test solution, 7 ml of acetate buffer pH 4, 1 ml of 1% ammonium molybdate in 0.05 N sulfuric acid and 1 ml of 0.25% freshly prepared ascorbic acid. The isobutanol extraction method was carried out as modified by WEIL-MALHERBE[7]. Color comparisons were made in a KLETT-SUMMERSON photoelectric colorimeter.

RESULTS

Interference by polymetaphosphate in the estimation of orthophosphate by the isobutanol extraction method

Increasing amounts of a sample of polymetaphosphate with average molecular weight 14,200 were added to 5 μg of orthophosphate and color was developed. There was no interference even at concentrations of metaphosphate-phosphorus as high as 600 times that of the orthophosphate.

Influence of the lower condensed phosphates on the color development of orthophosphate by the LOWRY-LOPEZ *method*

Linear condensed phosphates. Preneutralized pyrophosphate and tri-and tetrapolyphosphates were added in increasing amounts to 10 μg of orthophosphate and the color was measured after 15 and 30 min at room temperature (25–28°). All these samples contained a small proportion of orthophosphate.

TABLE I

INFLUENCE OF THE LOWER LINEAR CONDENSED PHOSPHATES ON THE COLOR DEVELOPMENT OF 10 μg ORTHOPHOSPHATE BY THE LOWRY-LOPEZ METHOD

	Phosphorus equivalent of condensed phosphate added μg	*Colorimeter reading*	
		15 min	*30 min*
Pyrophosphate	Nil	56	56
	100	56	55
	200	58	58
	400	61	61
	500	63	63
	600	62	62
	700	33	45
	800	18	28
	900	5	10
	1000	0	0
Tripolyphosphate	Nil	60	60
	1000	78	80
	2000	95	98
	3000	48	71
	4000	5	13
Tetrapolyphosphate	Nil	58	58
	200	74	78
	400	82	90
	600	86	104
	800	90	108
	1000	64	115
	2000	4	21

As seen from Table I pyrophosphate did not inhibit the color development till the ratio of pyrophosphate-phosphorus to orthophosphate was 50 : 1—60 : 1. Above this level there was progressive inhibition. When the pyrophosphate-phosphorus was 100-fold that of orthophosphate the inhibition was practically complete. Tripolyphosphate had less effect than pyrophosphate. Tetrapolyphosphate was more inhibitory than tripolyphosphate, but less so than pyrophosphate. In all cases the inhibition was partly overcome on storage of the developed color for 30 min, as indicated by the higher colorimetric readings.

Cyclic metaphosphates. Trimeta- and tetrametaphosphates at concentrations corresponding to over 5000 μg of phosphorus did not inhibit the color due to 5–20 μg of orthophosphate.

Effect of polymetaphosphates of varying molecular weights on the Lowry-Lopez *estimation*

A number of polymetaphosphates, with average molecular weights ranging from 1,500 to 16,000, were tested for their influence on the color development due to orthophosphate.

TABLE II

INFLUENCE OF THE POLYMETAPHOSPHATES ON THE COLOR DEVELOPMENT OF 10 µg ORTHOPHOSPHATE BY THE LOWRY-LOPEZ METHOD

	Phosphorus equivalent of condensed phosphate added *µg*	*Colorimeter reading*	
		15 min	*30 min*
1. Polymetaphosphate, weight-average molecular weight 1545; orthophosphate content by the Berenblum-Chain method = 9.16% of total phosphate.	Nil	57	59
	100	117	117
	200	158	167
	300	115	220
	400	72	180
	1000	10	31
	1500	0	11
2. Polymetaphosphate, weight-average molecular weight 2045; orthophosphate content by the Berenblum-Chain method = 3.37% of total phosphate.	Nil	58	
	50	67	
	100	68	
	150	63	
	200	36	
	400	29	
	600	17	
	800	14	
	1000	11	
3. Polymetaphosphate, weight-average molecular weight 3400; orthophosphate content by the Berenblum-Chain method = 0.85% of total phosphate.	Nil	60	60
	50	62	63
	100	65	66
	150	65	70
	200	50	71
	400	38	75
	600	34	77
	800	31	81
	1000	20	76
4. Polymetaphosphate, weight-average molecular weight 5600; orthophosphate content by the Berenblum-Chain method = 0.5% of total phosphate.	Nil	60	65
	100	62	73
	200	51	78
	300	45	78
	400	42	82
	600	40	77
	800	47	87
5. Polymetaphosphate, weight-average molecular weight 8200; orthophosphate content by the Berenblum-Chain method = 0.5% of total phosphate.	Nil	57	60
	50	29	55
	100	16	26
	150	12	19
	200	10	15
	400	7	9
	600	6	8
	800	6	8
	1000	4	7

TABEL II (continued)

	Phosphorus equivalent of condensed phosphate added µg	*Colorimeter reading*	
		15 min	*30 min*
6. Polymetaphosphate, weight-average molecular weight 14,200; orthophosphate content by the BERENBLUM-CHAIN method = 0.43% of total phosphate.	Nil	63	
	50	63	
	100	63	
	150	50	
	200	38	
	300	26	
	400	19	
	500	15	
	1000	7	
7. Polymetaphosphate, weight-average molecular weight 16,700; orthophosphate content by the BERENBLUM-CHAIN method = 0.52% of total phosphate.	Nil	57	60
	50	26	50
	100	14	28
	150	15	26
	200	8	19
	400	7	10
	600	6	7
	800	5	6
	1000	3	6

As seen from Table II all the polymetaphosphates inhibited more powerfully than the lower linear condensed phosphates. There seemed to be no correlation between the degree of inhibition and the molecular weight of the samples.

Orthophosphate estimation in the dialyzate of polymetaphosphates by the LOWRY-LOPEZ *and the* BERENBLUM-CHAIN *methods*

10-ml aliquots of 1% solutions of polymetaphosphates were dialyzed against 80 ml of distilled water in the cold for 24 h. Analysis of the dialyzate indicated the presence of significant amounts of orthophosphate by the LOWRY-LOPEZ method even though the original solutions had given negative tests. The results by the BERENBLUM-CHAIN method agreed closely with those by the LOWRY-LOPEZ method. It may be pointed out that the concentration of condensed phosphate in the dialyzate was less than 30-fold that of orthophosphate.

Influence of time, temperature and ammonium molybdate concentration

A sample of polymetaphosphate with an average molecular weight of 14,200 was taken as a typical example. Ten µg of orthophosphate were mixed with 5000 and 1000 µg of metaphosphate-phosphorus. The color was developed as usual and the readings were observed at 15 min intervals. The color intensity gradually increased, reached a maximum and remained fairly constant at the end of about 90 min. This colorimeter reading corresponded to the total orthophosphate present. A solution containing 1000 µg of polymetaphosphate-phosphorus, but no added orthophosphate, yielded a color maximum after 90 min which corresponded to its orthophosphate content estimated by the isobutanol extraction method. Increasing the temperature from 27 to 37°, or the ammonium molybdate concentration from 1.0 to 1.5%, did not significantly alter the color maxima at the end of 15 min.

Influence of added copper ions

The sample of polymetaphosphate was the same as in the previous experiment. The color was developed at 25° in the presence of known amounts of copper sulfate, keeping the final volume constant.

TABLE III

INFLUENCE OF COPPER IONS ON THE COLOR DEVELOPMENT OF ORTHOPHOSPHATE IN THE PRESENCE OF METAPHOSPHATE BY THE LOWRY-LOPEZ METHOD

Final concn. of copper sulfate *M*	*Orthophosphate added* *µg*	*Phosphorus equivalent of polymetaphosphate added* *µg*	*Colorimeter reading*	
			15 min	*30 min*
1) $4.2 \cdot 10^{-6}$	10	Nil	65	65
	10	500	76	77
	10	1000	76	89
	Nil	1000	23	26
2) $8.4 \cdot 10^{-6}$	10	Nil	63	65
	10	500	74	76
	10	1000	75	86
	Nil	1000	21	21
3) $1.68 \cdot 10^{-5}$	10	Nil	70	70
	10	500	84	85
	10	1000	83	85
	Nil	1000	20	20
4) $2.94 \cdot 10^{-5}$	10	Nil	70	73
	10	500	85	87
	10	1000	84	86
	Nil	1000	21	23
5) $4.2 \cdot 10^{-5}$	10	Nil	73	76
	10	500	88	90
	10	1000	84	88
	Nil	1000	21	24

The data (Table III) show that the inhibition due to polymetaphosphate tended to be overcome by the addition of copper ions. When 500 µg of metaphosphate-phosphorus was present along with 10 µg of orthophosphate, the addition of $4.2 \cdot 10^{-6}$ *M* copper sulfate over came the inhibition. However, when 1000 µg of metaphosphate-phosphorus was present the inhibition was not completely overcome in 15 min even when the copper sulfate was increased to $4.2 \cdot 10^{-5}$ *M*. At high concentrations of copper sulfate ($4.55 \cdot 10^{-3}$ *M*) the intensity of the color of the orthophosphate standard increased abruptly and then decreased with time.

Influence of metal ions other than copper

Since the metaphosphate solution was irradiated in a stainless steel vessel, and traces of metal might be dissolved, the influence of iron, nickel and chromium on the color development of orthophosphate in the presence of polymetaphosphate was tested. Nickel ($9.1 \cdot 10^{-5}$ *M*) accelerated the color development, but the inhibition was not completely overcome. At a concentration of $4.55 \cdot 10^{-4}$ *M* of nickel, 10 µg of orthophosphate could be estimated in the presence of 500 µg polymetaphosphate-phosphorus, but 1000 μg of metaphosphate-phosphorus interfered. Ferric ions ($9.1 \cdot 10^{-5}$ M) did not accelerate the color development but at a concentration of $1.82 \cdot 10^{-4}$ M, they also partially overcame the inhibition. Ferric ions at a concentration of $4.55 \cdot 10^{-4}$ M allowed the estimation of 10 μg of orthophosphate in the presence of 500 μg but not 1000 μg of polymetaphosphate-phosphorus. Ferrous ion ($9.1 \cdot 10^{-5}$ M) reduced the phosphomolybdate. Chromium had practically no effect even at $4.55 \cdot 10^{-4}$ M.

DISCUSSION

The presence of interfering materials in tissue extracts was noted by LOWRY AND LOPEZ[4]. Powerful inhibition has since been shown to be associated with liver, brain and bacterial extracts[8]. BRUEMMER AND O'DELL[9] and PEEL AND LOUGHMAN[8] independently and simultaneously discovered that the addition of minute quantities of copper ions helped to overcome these interferences. The former workers[9] suggested that the interference in liver extracts is due to sulfhydryl compounds and that copper ions promote their atmospheric oxidation to inactive disulfide derivates. On the other hand, PEEL AND LOUGHMAN[8] suggested that copper, which is always present as a contaminant in the reagents, is essential as an intermediate electron acceptor to bring about the reduction of phosphomolybdate by ascorbic acid. The various inhibitors function by binding the copper ions.

Results obtained by the present authors show that high concentrations of the linear lower and, more so, higher condensed phosphates inhibit the color development of small amounts of orthophosphate by the LOWRY-LOPEZ method. The cyclic metaphosphates, used in similar concentrations, do not inhibit. The fact that orthophosphate can be estimated quantitatively in the dialyzates obtained from the polymetaphosphates may be attributed to the fact that the dialyzates contain lower molecular compounds, which are less inhibitory and that the concentration of the condensed phosphate is low.

The inhibition due to polymetaphosphates is overcome, either partially or completely, by the addition of copper and other metal ions. PEEL AND LOUGHMAN[8] considered that the effect of copper is a specific one and that it cannot be replaced by other ions in comparable concentration. The present investigation shows that low concentrations of nickel and higher concentrations of iron are also effective in overcoming the inhibition due to polymetaphosphate. The addition of copper to allow the assay of orthophosphate in the presence of metaphosphate cannot be recommended as a routine practice, since the inhibition is not overcome quantitatively at higher concentrations of polymetaphosphate.

ACKNOWLEDGEMENT

The authors are grateful to Professor A. C. CHATTERJI and Mr. H. N. BHARGAVA for the supply of synthetic metaphosphates. One of us (K. K. T.) thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a fellowship.

SUMMARY

The linear condensed phosphates inhibit the development of color due to orthophosphate by the method of LOWRY AND LOPEZ. The higher members of the series (the polymetaphosphates) have more effect than the lower members (pyrophosphate, tripoly- and tetrapolyphosphates). The two cyclic metaphosphates, trimeta- and tetrametaphosphate, do not inhibit. The inhibition by

polymetaphosphate is partly overcome by storing the developed color for about 90 min. Low concentrations of copper and nickel and higher concentrations of iron(III) remove either partially or completely the inhibition due to polymetaphosphates. None of the metaphosphates interferes in the estimation of orthophosphate by the isobutanol extraction method of Berenblum and Chain.

RÉSUMÉ

Une étude a été effectuée sur le dosage colorimétrique de l'orthophosphate en présence des phosphates condensés, par la méthode de Lowry-Lopez. On a examiné également l'influence de traces de cuivre et d'autres cations sur le dosage.

ZUSAMMENFASSUNG

Der störende Einfluss von Polyphosphaten auf die colorimetrische Bestimmung der Orthophosphate nach Lowry-Lopez kann durch kleine Mengen Kupfer, Nickel oder Eisen(III) weitgehend ausgeschaltet werden.

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PYROMELLITEIN INDICATORS

I. ACID–BASE INDICATORS CONTAINING FOUR CONDENSED PHENOLIC GROUPS

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In 1906 Silberrad[1–3] reported the preparation of dyes formed by condensation of phenol and of resorcinol with pyromellitic dianhydride to give materials which he suggested could be used as dyes with mordants.

While such compounds are possible indicators, since they resemble phenolphthalein and fluorescein in their structures, no attempt seems to have been made to use them as such since that time. The dianhydride structure should permit the preparation of two very interesting groups of compounds, since it is possible to condense two or four phenolic groups. There is also the possibility of making "internally mixed" indicators by condensing two different phenols with the dianhydride.

In preparing such compounds the author has found that it is much easier to obtain clearly defined pure compounds containing four condensed phenolic groups and the present paper is concerned with them. More work is being done on the purification of compounds containing two condensed phenolic groups, and a report on this will be presented later.

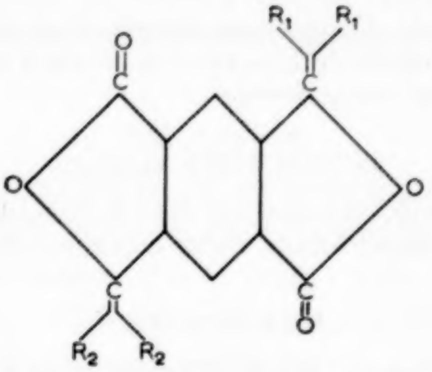

Fig. 1. Structure of pyromellitein indicators.

Indicators containing four phenolic groups of the same kind may be prepared by the usual methods for making phenolphthalein and resorcinol. When 8-hydroxy quinoline was used, it was necessary to precipitate the indicator at a pH of about 7 since it is soluble in both acids and bases, as was the case also with the condensation product with dimethyl aniline.

In testing these compounds for use as indicators, a titration was carried out using a Fisher titrimeter, the pH range and color change being noted. Samples were prepared using buffers for use in determining the transmission minima using a Beckman spectrophotometer, Model B. These results are summarized in Table I.

TABLE I

OPTICAL PROPERTIES OF PYROMELLITEIN INDICATORS (VISIBLE LIGHT)

R_1	R_2	*Color change*	*pH-range*	*Maximum absorption Å*
Phenol	Phenol	C-pink	10.3–12	5600
Oxine	Oxine	Y-Gr. (1)	10–11.5	6400 and 3700 (Green)
c-ClC_6H_4OH	o-ClC_6H_4OH	C-purple	9–10.9	5750
Resorcinol	Resorcinol	Pink-red	Red above 8	4600-pH 5 5000-above pH 8
Phenol	Resorcinol	Pink-red	Red above 6 (2)	4600-pH 5 4900-above pH 6
DiMeAniline	DiMeAniline	Y-Blue (3)	4–5.6	6200 (4)

1. Decrease in transmission to pH 11.5, then increase at pH 12.
2. Sudden brightness at pH 6 in visible light.
3. Sudden change at pH 4.5 going from acid to base. CO_2 interferes in base to acid.
4. Pronounced decrease in transmission below 4500 Å at all pH values.

Since some of these compounds showed fluorescence under ultraviolet light, a titration was carried out using the titrimeter along with a shielding arrangement so that the solution was exposed to ultraviolet light and shielded from daylight. Since it could be seen visually that the fluorescing indicators showed fluorescence to blue light, the maximum for the emitted fluorescent light was determined by a differential method using the Beckman. This consisted of determining the light transmission twice by the method usually used with this instrument, except that on the first run a blue filter was placed ahead of the sample cells (including the water cell), and on the second run the same blue filter was put after the sample cells. The difference was a measure of the amount of fluorescence. The method was checked using dichlorofluorescein. What is obtained is not an absolute measure of the fluorescence but simply the maximum of the fluoresced light. Results are shown in Table II.

TABLE II

FLUORESCENT PYROMELLITEIN INDICATORS (2)

R_1	R_2	*Color change (1)*	*pH-range*	*Emission maximum*
Resorcinol	Resorcinol	Y-Fl. Gr.	0.6–2	480
Phenol	Resorcinol	Y-Fl. Gr.	1.9–4	480

1. Under near ultraviolet light.
2. The DiMeAniline and oxine compounds also showed slight blue fluorescence from pH 1–12.

The data presented in this paper were obtained in dilute solution by titrating carbonate free NaOH with HCl, both solutions being about 0.1 *N*. The polyprotic nature of these indicators make it very probable that there will be pronounced salt effects, which are yet to be determined. The oxine condensation compounds are of particular interest since they contain not only acid hydrogens but are capable of forming complexes through the nitrogen of the oxine. Particular attention will be paid to these compounds in future studies of salt effects.

ACKNOWLEDGEMENTS

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SUMMARY

A series of indicators have been prepared by condensing pyromellitic dianhydride with various phenols. Color changes and pH ranges have been determined, both in visible light and in ultraviolet light, for those indicators that fluoresce. Of particular interest is the indicator prepared using oxine as the phenolic compound, since there is a possibility in this case of complex formation through the nitrogens of the condensed oxine groups.

RÉSUMÉ

Une série d'indicateurs ont été préparés par condensation du dianhydride pyromellitique avec divers phénols. Les pH de virage et les changements de colorations ont été déterminés.

ZUSAMMENFASSUNG

Die Kondensationsprodukte von Pyromellitsäure-dianhydrid mit verschiedenen Phenolen eignen sich als Indikatoren. Die pH Werte der Umschlagspunkte und die Farbänderungen werden angegeben.

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A RAPID METHOD FOR THE DETERMINATION OF ORGANIC CARBON IN SOIL

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INTRODUCTION

In 1927 SCHOLLENBERGER[1] proposed treating the soil with dichromate instead of permanganate and, since then, this method has tended increasingly to replace the wet combustion with permanganate. Various modifications of the dichromate oxidation have been proposed, some of which give low results compared with dry combustion and therefore require empirical conversion factors. Such unsatisfactory results must be attributed either to a desire to simplify the analysis, or to the choice of unfavourable conditions.

The modification of KURMIES[2] has been proved reliable (MEBIUS *et al.*[3]), but it would be improved if a reliable indicator could be found for direct titration of the surplus of dichromate with Mohr's salt. In the procedure of KURMIES an excess of ferrous salt is added and is titrated with permanganate, no indicator being used. It requires some experience to decide the end-point. In a recent paper SIMAKOV[4] suggests a solution of N-phenylanthranilic acid; his claim of a very sharp and clear end-point has been confirmed by us.

However SIMAKOV does not use the KURMIES modification but the simpler method of TIURIN[5], which often gives low values compared with those of the elementary analysis. We therefore decided to check the procedure of TIURIN-SIMAKOV and to try to improve it to give full agreement with the dry combustion. However, chlorides can interfere, since CrO_2Cl_2, formed as an intermediate with chloride-containing soils and boiling at 117°, can evaporate at the reaction temperature of *ca.* 150°. In such cases SIMAKOV and some others[6] add Ag_2SO_4. The KURMIES oxidation, performed at *ca.* 100°, avoids this complication. We therefore advise the KURMIES method for all saline soils, though the application of a reflux condenser, as proposed by us, might perhaps retain most of the CrO_2Cl_2 vapours.

EXPERIMENTAL

The errors of the procedure of TIURIN-SIMAKOV and other modifications of the dichromate oxidation are probably due to a. amount of sulphuric acid used, b. time of boiling, c. correctness of the blanks, or d. soil/reagent proportion. We therefore investigated these factors.

Influence of the amount of sulphuric acid

In these experiments, 0.1–0.5 g of the dried and ground soil was placed in 100-ml Erlenmeyer flasks. The required amount of conc. sulphuric acid and 10 ml of a 0.4 *N* solution of dichromate in 62% (w/v) sulphuric acid were added and, after attaching a reflux-condenser, the mixture was boiled for half an hour on an electric sand-bath. After cooling and rinsing the condenser with water, 3 to 5 drops of the N-phenylanthranilic acid were added and the titration performed with a 0.2 *N* solution of Mohr's salt at room temperature. With the addition of one drop, the colour shifted from violet to bright green. A blank determination was run simultaneously. The results with a clay soil are presented in Table I and also graphically in Fig. 1.

TABLE I

INFLUENCE OF SULFURIC ACID ON THE ORGANIC-CARBON DATA

ml conc. sulfuric acid added per determination	*ml 0.2 N Mohr's salt per determination*	*ml 0.2 N Mohr's salt per blank determination*	% C *in air-dry soil*	% C *in the dry matter of the soil*
0	13.16	20.19	2.11	2.17
1	12.59	20.16	2.27	2.34
3	11.45	20.08	2.59	2.66
4	10.91	20.03	2.74	2.82
5	10.65	19.85	2.76	2.84
6	10.27	19.45	2.75	2.83
7	9.87	18.96	2.73	2.81
8	9.26	18.22	2.69	2.77

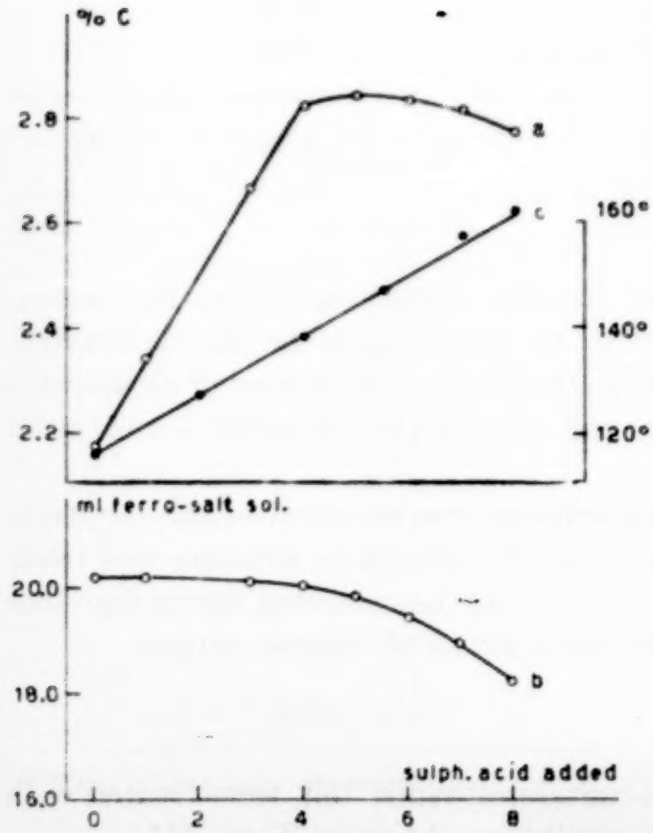

Fig. 1. Influence of quantity of sulphuric acid upon: a = % C, b = blank, c = boiling point (mean).

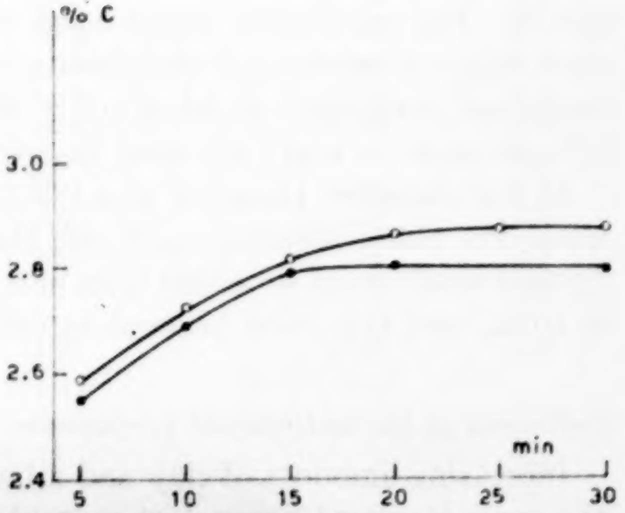

Fig. 2. Influence of the boiling time. o = clay soil, ● = sandy soil.

These figures show clearly that an addition of *ca.* 5 ml of conc. sulfuric acid is the optimum for this reaction, and that the procedure proposed by TIURIN gives results that are much too low.

Influence of the time of boiling

A clay soil and a sandy soil with a rather high humus-content were used. The sand-bath had of course to be heated to the desired temperature before the start. The results are shown in Fig. 2. It is evident that 20 min boiling is sufficient but, for the sake of safety, 30 min was used in the standard procedure.

Influence of the blank determination

A difficult point with the dichromate methods is the partial decomposition of dichromate during boiling; it is thus necessary to apply a correction factor. Blanks with and without boiling were determined with 0.2 and 0.4 *N* dichromate. The concentration of sulfuric acid, the total volume, and the boiling time were the same as for all normal blanks. The results are shown in Table II.

TABLE II

INFLUENCE OF THE CONCENTRATION OF DICHROMATE IN BLANKS ON THE LOSS DURING BOILING

	ml 0.2 N Mohr's salt titrated					
	10 ml 0.4 N dichromate			*10 ml 0.2 N dichromate*		
	not boiled	*boiled*	*difference*	*not boiled*	*boiled*	*difference*
Expt. 1	20.26	19.85	0.41	10.13	9.96	0.17
Expt. 2	20.26	19.74	0.52	—	9.82	0.31
Expt. 3	—	19.83	0.43	—	9.89	0.24
mean	20.26	19.80	0.46	10.13	9.89	0.24

It is evident that the loss of dichromate depends approximately on its concentration. The correction added must therefore be proportional to the dichromate used. Since 10 ml of 0.4 *N* dichromate is used in the blanks, for each ml of dichromate consumed (expressed as ml of 0.2 *N* Mohr's salt used in the titration) a correction of $0.46/20.26 = 0.023$ ml must be added.

If, for example, 10.00 ml of 0.2 *N* ferrous solution was required in the titration, while the blank required 19.80 ml, then 9.80 ml of dichromate solution was used. To this result must be added $9.80 \times 0.023 = 0.22$ ml; the corrected figure therefore is 10.02, and this must be used to calculate the content of organic carbon.

Influence of the soil/reagent proportion

Increasing amounts of clay and a humus-containing sandy soil, were treated with the same standard amount of reagent; the results are shown in Table III.

The influence of varying amounts was not altogether negligible. However, if the soil consumes 5–10 ml of dichromate, the results may be considered correct.

TABLE III

INFLUENCE OF SOIL/REAGENT PROPORTION

Soil taken (mg)	*Sandy soil*		*Clay soil*	
	0.2 N dichromate consumed (ml)	*% C*	*0.2 N dichromate consumed (ml)*	*% C*
100	4.64	2.78	2.94	1.76
200	9.18	2.75	5.84	1.75
300	13.77	2.75	8.70	1.74
400	—	—	11.46	1.72
500	—	—	14.18	1.70

Reproducibility

The standard deviation, S.D. of an individual estimate can be calculated from any series of duplicate analyses by means of the formula S.D. $= \sqrt{\Sigma\Delta^2/2n}$, where Δ denotes the difference between the duplicates and n is the number of samples in the series. From a series of 14 such determinations (whose means ranged from 1.45 to 7.68, with an average of 2.86) a value of S.D. = 0.034 was found. This represents a standard deviation of 1.2% for a single analysis.

Comparison of the method with the standard (dry combustion) method

The average carbon content of the 14 samples mentioned above was 2.861% according to the dichromate method and 2.856% according to dry combustion. The difference is clearly negligible.

Statistical analysis of the relevant data, which are assembled in Table IV, confirms this.

TABLE IV

COMPARISON OF THE RESULTS

Sample no.	*% C*		*difference*	
	dichromate method[a]	*elem. analysis*[a]	*absolute*	*in %*
1	2.83	2.82	+0.01	0.4
2	1.99	2.03	—0.04	2.0
3	2.94	2.97	—0.03	1.0
4	3.66	3.58	+0.08	2.2
5	2.56	2.63	—0.07	2.7
6	2.33	2.32	+0.01	0.4
7	2.45	2.48	—0.03	1.2
8	1.98	2.06	—0.08	4.0
9	2.91	2.92	—0.01	0.3
10	1.45	1.47	—0.02	1.4
11	2.67	2.60	+0.07	2.6
12	2.86	2.77	+0.09	3.2
13	7.68	7.52	+0.16	2.1
	(7.69)	—	—	—
14	1.74	1.82	—0.08	4.6
mean	2.86	2.85		

[a] Mean of duplicate determinations.

Conclusions

The above tests justify the conclusion that the method can be used for routine determinations of organic carbon in soil. The method is easier, quicker and cheaper than elementary analysis or the KURMIES method, and in ordinary soils of all types it is as accurate. Saline soils and those containing inorganic oxidizable substances (FeS; FeS_2; Fe^{+2}, Mn^{+2}, etc.) must be excluded; dry combustion is then the only fully reliable method.

RECOMMENDED PROCEDURE

Reagents

A 0.267 *N* solution of $K_2Cr_2O_7$ (13.072 g of $K_2Cr_2O_7$ and 550 ml of conc. sulfuric acid in distilled water, diluted to 1 l).
Sulfuric acid 95–97% ($d = 1.84$). A 0.2 *N* solution of Mohr's salt (78.390 g of $(NH_4)_2SO_4.FeSO_4{\cdot}6H_2O$ and 50 ml conc. sulfuric acid in distilled water, diluted to 1 l). The indicator used by SIMAKOV[7]: 200 mg of N-phenylanthranilic acid dissolved in an 0.2% Na_2CO_3 solution.

Procedure

Weigh 0.1 to 0.5 g (depending on the estimated C-content) of the finely ground soil into an Erlenmeyer flask of 100 ml; add 15 ml (exactly) of the dichromate reagent, connect the flask by a glass joint with a reflux condenser, and boil for 30 min on an electrically heated sand-bath. Cool the flask in water, while still connected to the condenser, and then rinse the latter with water. Titrate with Mohr's salt solution at room temperature, adding 3 drops of the indicator. As the end-point is approached a few more drops of the indicator must be added. The colour change is from violet to bright green. A blank analysis must be run in exactly the same way.

The difference between the blank and the soil analysis must be corrected as explained on p. 122. From this corrected value, *A*, the content of organic carbon, expressed as % by weight of the soil, can be calculated from the expression:

$$\frac{A \times 0.2 \times 0.003 \times 100}{\text{g soil}} = \%\ \text{C}$$

ACKNOWLEDGEMENT

The author is grateful to Dr. G. W. HARMSEN for his interest in this work.

SUMMARY

TIURIN's method for the determination of organic carbon in soil is modified to give results practically identical with those of the dry combustion method. The standard deviation of a single determination is only 1.2%. By using 50 mg of soil and 10 ml of 0.2 *N* dichromate solution, soils with a carbon content up to 12% can be analyzed. The method is suitable for all soils except those containing much chloride or reducing substances other than organic carbon. Carbonates do not interfere.

RÉSUMÉ

Une modification de la méthode de TIURIN est proposée pour le dosage du carbone organique dans les terres. On peut obtenir ainsi des résultats pratiquement identiques à ceux fournis par la méthode de combustion par voie sèche.

ZUSAMMENFASSUNG

Es wird eine Modifikation der Methode von TIURIN zur Bestimmung des organisch gebundenen Kohlenstoffs in Bodenproben beschrieben, die praktisch die gleichen Resultate ergibt, wie sie durch die trockene Verbrennungsmethode erhalten werden.

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DETERMINATION OF IRON IN WINE USING 2,4,6-TRIPYRIDYL-s-TRIAZINE

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The first use of the now well known colorimetric reagent for iron, 1,10-phenanthroline, was for the determination of iron in wine (SAYWELL AND CUNNINGHAM[1]) and its use has become more or less standard, the various procedures which have been proposed differing primarily in the method used to decompose the sample prior to color development. Usually, the organic material present is destroyed by a wet ashing with nitric and perchloric acids or with hydrogen peroxide. However, BANICK AND SMITH[2], utilizing the supersensitive iron reagent, bathophenanthroline, eliminate the usual wet ashing and extract the red iron(II) bathophenanthroline compound directly into isoamyl alcohol.

A new ferroine reagent, 2,4,6-tripyridyl-*s*-triazine (TPTZ), has recently been introduced as an extremely sensitive reagent for the colorimetric determination of iron[3]. This reagent possesses many of the advantages of bathophenanthroline and is much easier to prepare. TPTZ reacts with iron(II) to give an intensely violet colored, water soluble ion, $Fe(TPTZ)_2^{+2}$. In the presence of perchlorate, the iron(II) derivative can be extracted into nitrobenzene. The molar extinction coefficients are 22,600 at 593 mμ in aqueous solution and 24,100 at 595 mμ in nitrobenzene. The permissible pH range is 3.4 to 5.8 in aqueous solution and when the extraction into nitrobenzene is used, the pH range is increased to 2.7 to 7.0. The color conforms to Beer's law in both solvents.

The object of the present work was to develop a suitable procedure for the determination of iron in wine using TPTZ and taking advantage of the extraction feature to eliminate the wet ashing step.

RECOMMENDED PROCEDURE

Reagents

2,4,6-Tripyridyl-s-triazine (*TPTZ*). 0.001 *M*. Dissolve 0.312 g of TPTZ (synthesized by the method of CASE AND KOFT[4]; available from the G. Frederick Smith Chemical Co., Columbus, Ohio) in a few drops of hydrochloric acid and dilute to 1 l with water.

Hydroxylammonium chloride. 10%. Dissolve 100 g of hydroxylammonium chloride in 900 ml of water. To remove iron add 10 ml of 0.001 *M* TPTZ and 1 g of sodium perchlorate and extract with 25 ml of nitrobenzene.

Sodium acetate–acetic acid buffer. Prepare a solution 2 *M* in acetic acid and 2 *M* in sodium acetate by dissolving 115 ml of acetic acid and 164 g of sodium acetate in water and diluting to 1 l. To remove iron, add 10 ml of 10% hydroxylammonium chloride, 10 ml of 0.001 *M* TPTZ, and 1 g of sodium perchlorate and extract the solution with 25 ml of nitrobenzene.

Sodium perchlorate. 10%. Dissolve 100 g of sodium perchlorate in 900 ml of water and remove iron in the same way as with the acetate buffer.

Standard iron solution. Dissolve 0.2500 g of electrolytic iron in 20 ml of hydrochloric acid and dilute to exactly 1 l. Pipet 100.0 ml of this solution into a 1-liter volumetric flask, add 10 ml

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of hydrochloric acid and dilute to volume with water. Dilute 100.0 ml of this solution and 10 ml of hydrochloric acid to exactly 1 l to give a solution containing 2.50 μg of iron per ml.

Preparation of calibration curve

Pipet various volumes from 0 to 15 ml of a solution containing 2.50 μg of iron per ml into 125-ml separatory funnels. Add 2.0 ml of 10% hydroxylammonium chloride, 5.0 ml of 0.001 *M* TPTZ, 5.0 ml of acetate buffer and 1.0 ml of 10% sodium perchlorate to each funnel. Extract each solution three times using 4.0-, 2.0- and 2.0-ml portions of nitrobenzene. Collect the extracts of each solution in a 10-ml volumetric flask, dilute to volume with ethanol and determine the absorbancy at 595 mμ using 1-cm cells.

Procedure for determination of iron with preliminary wet ashing.

Pipet a 3.00-ml sample of wine into a 250-ml conical flask fitted with a reflux head. Add 10 ml of nitric acid and 5 ml of perchloric acid and heat to fumes of perchloric acid. Cool the solution, add 20 ml of water and heat to boiling to remove any chlorine. After cooling the solution, add 2.0 ml of 10% hydroxylammonium chloride, 2.0 ml of acetate buffer and 5.0 ml of 0.001 *M* TPTZ. Neutralize the solution with ammonium hydroxide to pH 4 to 5 using a pH meter or pH indicating paper. Transfer the solution to a 125-ml separatory funnel, add 4.0 ml of nitrobenzene and shake vigorously for 1 min. Allow the phases to separate and gently swirl to remove drops of nitrobenzene clinging to the upper walls of the funnel. Repeat the extraction using two 2.0-ml portions of nitrobenzene. Collect the extracts in a 10-ml volumetric flask, dilute to volume with ethanol and measure the absorbancy at 595 mμ using 1-cm cells. Run a blank through the entire procedure and subtract its absorbancy from the absorbancy of each of the other solutions.

Procedure for the direct determination of iron

To a 3.00-ml sample of wine contained in a 100-ml beaker add 2.0 ml of 10% hydroxylammonium chloride, 5.0 ml of ethanol, 5.0 ml of acetate buffer and 5.0 ml of 0.001 *M* TPTZ. Heat the solution to boiling for 5 min, cool and transfer to a 125-ml separatory funnel. Wash the beaker with 20 ml of ethanol and 1.0 ml of 10% sodium perchlorate and add the washings to the separatory funnel. Extract the solution three times using one 4.0-ml and two 2.0-ml portions of nitrobenzene and collect the extracts in a 10-ml volumetric flask. Dilute to volume with ethanol and determine the absorbancy of the solution at 595 mμ using 1-cm cells. Run a blank through the entire procedure and subtract its absorbancy from the absorbancy of the sample solution.

RESULTS AND DISCUSSION

The iron content of several wines was determined using TPTZ in both the direct extraction and wet ashing procedures and also by 1,10-phenanthroline following wet ashing. The wine samples were obtained through retail outlets and were of U.S. and European vintage. All determinations were carried out in at least triplicate. The results are shown in Table I.

It is apparent that the determination of iron in wine by the direct TPTZ method usually, but not always, gives values which are lower than those obtained by wet ashing procedures. This is presumably due to the presence of a very stable iron compound which is not broken by TPTZ. If this is the case, it may well be that the "complexed iron" is inactive in forming a turbidity in wine and that the results obtained for "uncomplexed iron" by this direct method may be more useful to the wine producer than a knowledge of the total iron content. Various conditions, such as length of heating and ethanol concentration, were changed; but in no case was it possible to completely recover the iron from certain wines using the direct procedure. The iron which is not recovered remains in the aqueous phases as shown in one case by a wet ashing of the remaining water solution.

The iron content of the Medoc Bordeaux Red Wine was also determined by the direct method of BANICK AND SMITH and found to be 6.46 mg of iron per l, almost identical with the direct TPTZ method.

The procedure employing preliminary wet ashing followed by determination of the iron with TPTZ does have distinct advantages over the usual 1,10-phenanthroline methods. A smaller sample may conveniently be used due to the increased sensitivity of the reagent and the extractability of the iron derivative into nitrobenzene. Iron may be easily removed from the reagents and the blank reduced to essentially zero. Also, it is unnecessary to remove the excess perchloric acid as is the case in the determination employing 1,10-phenanthroline.

TABLE I

DETERMINATION OF IRON IN WINE USING TPTZ

(Each result given is the average of at least three determinations)

Wine	*Wet ashing 1,10-phenanthroline*		*Wet ashing TPTZ*		*Direct TPTZ*	
	Fe found mg/l	*average deviation*	*Fe found mg/l*	*average deviation*	*Fe found mg/l*	*average deviation*
Italian Swiss Colony California Sherry	2.54	0.07			2.51	0.01
Meier's Ohio State Tawny-Port	3.79	0.15			3.80	0.04
Medoc Bordeaux Red Wine	7.53	0.10	7.56	0.04	6.44	0.03
Virginia Dare White Wine	4.42	0.01	4.48	0.01	4.16	0.08
Virginia Dare Red Wine	5.81	0.02	5.82	0.03	5.37	0.11
Ambassador California Burgundy	4.73	0.07	4.69	0.01	4.24	0.02
Richelieu California Port	5.15	0.01	5.12	0.02	4.68	0.01
Homestead Piestengel Rhubarb Wine	2.27	0.00	2.27	0.01	2.28	0.02

SUMMARY

Procedures are described for the determination of iron in wine using 2,4,6-tripyridyl-*s*-triazine, a new ferroine reagent. One procedure involving wet ashing with nitric and perchloric acids gives results comparable to those obtained using the usual 1,10-phenanthroline method while a direct extraction procedure often gives low but reproducible results indicating the presence of "complexed iron" in the sample.

RÉSUMÉ

Deux méthodes sont décrites pour le dosage du fer dans le vin au moyen d'un nouveau réactif, la 2,4,6-tripyridyl-*s*-triazine. On procède soit à une minéralisation par voie humide soit par extraction directe.

ZUSAMMENFASSUNG

Es werden zwei Methoden beschrieben zur Bestimmung des Eisens in Wein mit Hilfe von 2,4,6-Tripyridyl-*s*-triazin nach vorausgehender nasser Veraschung oder Extraktion.

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES

V. TIME AND TEMPERATURE FACTORS IN THE PRODUCTION OF INSOLUBLE SUBSTANCES

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(Received Juny 8th, 1959)

The effect of heat in changing the solubility of substances has been studied[1] and it has been shown that many substances which are soluble in acids under ordinary conditions are rendered difficultly soluble on heating for some time. In these studies only one temperature was taken for all substances. It was however possible that a critical temperature existed at which these substances began to be insoluble. A preliminary study of this problem has shown that substances which become difficultly soluble on heating generally begin to show changes in solubility after crossing a certain minimum temperature. Below this temperature the substance remains soluble however much it is heated. As the substances were heated at temperature intervals of 100° it is not possible to say whether there is a particular "critical temperature" but the data show conclusively that it is only after passing beyond a certain temperature range that each substance begins to change into the insoluble form.

TABLE I

Name of the compound	*Percentage left undissolved in one standard acid treatment heated for 2 h*								
	100°	*250°*	*300°*	*400°*	*500°*	*600°*	*700°*	*800°*	*900°*
1. Chromium phosphate	Soluble	26.2	52.0	75.4	78.2	85.0	90.2	95.0	95.0
2. Nickel chromite	←	Soluble		→45.2	94.5	96.0			98.0
3. Chromium arsenate	←	Soluble			→28.4	58.0	96.6	98.8	—
4. Cobalt antimonate	←	Soluble				→42.0	88.6	96.0	99.3
5. Nickel antimonate	←	Soluble				→40.2	87.0	96.0	99.8
6. Manganese antimonate	←	Soluble				→93.2	95.0	95.0	99.7
7. Cobalt tungstate	←	Soluble					→62.1	78.5	—

From Table I the critical temperature ranges of the following substances are:

(a) Chromium phosphate, 100–250°; (b) Nickel chromite, 300–400°; (c) Chromium arsenate, 400–500°; (d) Antimonates of nickel, cobalt and manganese, 500–600°; (e) Cobalt tungstate, 600–700°.

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After the critical temperature range has been passed the percentage of the substance rendered insoluble in a given time continues to increase with increase in temperature. In the case of chromium phosphate this increase is gradual and steady but in other cases the increase is less regular. If the temperature is kept constant above the critical range the percentage of the insoluble portion increases with increase in the period of heating (Table II).

TABLE II

Name of the compound	*Percentage left undissolved in one standard acid treatment*	
	2 h at 600°	*11 h at 600°*
1. Chromium phosphate	85.0	88.0
2. Cobalt antimonate	42.0	85.0
3. Nickel antimonate	40.2	60.5
4. Manganese antimonate	93.2	93.2
5. Chromium arsenate	58.0	80.0

A few experiments were also made to see how the time factor affects the change at the maximum temperature used; at temperatures much beyond the critical range the change in solubility is very rapid (Table III). Thus on heating the antimonates of nickel, cobalt and strontium and uranium chromite for 10 min at 900°, the substance attained almost its maximum insolubility.

TABLE III

Name of the compound	*Percentage left undissolved in one standard acid treatment*	
	10 min at 900°	*2 h at 900°*
1. Cobalt antimonate	98.5	99.3
2. Strontium antimonate	98.3	99.6
3. Nickel antimonate	99.0	99.8
4. Uranium chromite	95.6	96.0

SUMMARY

It has been shown that substances which become insoluble on heating begin to change into the insoluble form after passing beyond a certain range of temperature which is characteristic for each substance. Beyond this range the percentage of insoluble portion formed increases both with time and temperature. At temperatures much beyond the critical range the change into the insoluble form is very rapid.

RÉSUMÉ

Les auteurs ont effectué une étude systématique de substances insolubles. Dans cette cinquième partie, ils ont examiné l'influence de la température et de la durée de chauffage sur leur formation.

ZUSAMMENFASSUNG

Es wurde eine systematische Untersuchung der durch Hitzeeinwirkung entstehenden unlöslichen Verbindungen vorgenommen und der Einfluss von Temperatur und Erhitzungsdauer untersucht.

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GAS–LIQUID PARTITION CHROMATOGRAPHY

COLUMN BEHAVIOR AND ITS REPRODUCTION

CRITERIA FOR FAVORABLE COLUMN BEHAVIOR*

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In the present paper an attempt has been made to explain the movement and the distribution of a solute in a gas–liquid partition chromatographic (GLPC) column from probability considerations. It has been shown that the mechanism of movement of the solute is analogous to a BERNOULLI trial system. Repeated independent trials are known as BERNOULLI trials if there are only two possible outcomes for each trial and their probabilities remain the same throughout[1]. If $b(k, n, p)$ be the probability that n BERNOULLI trials with probabilities p for success and $q(= 1 - p)$ for failure result in k successes and $n-k$ failures, then

$$b(k, n, p) = \binom{n}{k} p^k q^{n-k} \quad \ldots \ldots \ldots \ldots \ldots \quad (1)$$

It is possible to attribute a "probability of success" term and a total number of "trials" term to any column–solute combination. The magnitude of these two terms, however, depends upon the operating conditions of the column and the nature of the solute. Once these two terms are specified, the "behavior" of the column is exactly defined. When these two terms are reproduced, the column behavior is also reproduced. It should be noted that the emphasis is laid upon reproducing the column "behavior" instead of duplicating the operating conditions individually. Conditions responsible for producing the most favorable column behavior for normal types of solutes have also been discussed from the viewpoint of the equilibrium distribution. The compounds having moderate polarities and heats of vaporization (obeying TROUTON's relation) are considered as normal solutes. Favorable column behavior is considered to be that one which is most suitable for the separation of certain specified groups of compounds.

Column behavior

It is now well established[2–5] that whatever may be the approach to explain the mechanism in the GLPC column causing the distribution of a solute, the distribution can always be expressed by one of the conventional covergent series like the binominal, POISSON, or GAUSSIAN.

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During the chromatographic analysis the three parameters of the distribution of the solute measured are (1) the emergence time or volume, (2) the width of the distribution curve at the point of inflection, and (3) the height of the peak. It will be seen shortly that the emergence time $R_t = f(n, v, p, F)$ and $w = g(n, v, p, F)$ of the same set of variables. In the two foregoing equations, n is the number of theoretical plates which corresponds to the number of trials in a BERNOULLI system; v is the plate dimension, p is the probability of success and F is the flow rate. In this particular case, the probability of success means the probability of finding a solute molecule in the gas phase: the event of entrance or exit of a solute molecule into or out of a plate corresponds to a trial. Thus the two fundamental conditions of the BERNOULLI theorem[1], (i) that there are only two possible outcomes for each trial and (ii) that all the trials are identical and independent, are fulfilled. The solute fraction, p, stays in the gas phase and moves and is successful. The fraction, q $(q = 1-p)$, stays in the stationary phase and is unsuccessful. When n is made large, using LAPLACE's approximation, the distribution can be expressed by a GAUSSIAN function and the width of the distribution curve depends on σ, the standard deviation. When p becomes infinitesimally small, *i.e.* by letting $p \to 0$ and $q \to 1$, and n is very large so that np is of moderate magnitude, the distribution becomes a POISSON function. In the case of GLPC, p is very small. In all the three types of distributions mentioned above, the height of the mean is the highest ordinate. Its value corresponds to the probability of finding the largest number of molecules at the particular trial, plate, or stage.

The situation in GLPC is a case of alternative probability (mutually exclusive events)[6] due to the constant value of partition coefficient. Mutually exclusive events mean that only one of them can happen and the happening of which automatically prevents the happening of the other. Due to the constancy of the partition coefficient, the presence of any one molecule in gas phase automatically prevents the presence of any other molecule, although the different molecules are indistinguishable. When a quantity m is introduced into the column, let p be the probability of a molecule being present in the gas phase; when introduced into the column, all the different identical molecules will have the same probability p of being present in the vapor phase, then the probability that any molecule will be in the gas phase is given by

$$P = p + p + p + \ldots \qquad (2)$$

depending upon how many molecules have been introduced into the column. In other words, the largest number of probable molecules to be found at a definite stage will be double, triple, quadruple, etc., corresponding to the multiples of m introduced into the column. Therefore, it follows that the height of the mean in the distribution curve is proportional to the quantity of solute introduced into the column.

That this relation (2) is true can be proved by means of a simple analogy. Suppose one is to find out the probability of throwing an even number with an ordinary six-sided die. The events to be considered are the throwing of a 2, a 4, or a 6, each of which has a probability of 1/6. These events are mutually exclusive, that is, the appearance of any one of these automatically prevents the appearance of any others. The probability of at least one of these numbers, that is, of an even number to show up, is $1/6 + 1/6 + 1/6 = 1/2$, and therefore

$$P = p + p + p +$$

Let us now assume the following:

1. The column is composed of a large number, n, (say $n = 100$) of equivalent plates serially numbered 0, 1, 2 . . . . . . n.

2. Each plate consists of a stationary phase of volume V_s and a gaseous phase of volume V_m.

3. One unit mass of the solute is introduced into the plate numbered zero within a very short time and the solute has a distribution coefficient

$$K = \left(\frac{C_s}{C_m}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where C_s and C_m are the concentrations in the stationary and the mobile phases.

4. Subsequent portions of the gaseous phase introduced into the plate zero in installments of V_m are solute free and move from 0 to n plate.

5. At each operation (trial) V_m volume of movable phase is passed onto the next plate.

The fraction p of the solute that moves out of each plate at each operation is given by

$$\begin{aligned} p &= \frac{V_m C_m}{V_m C_m + V_s C_s} \\ &= \frac{V_m}{V_m + K V_s} \\ &= \frac{V_m}{v} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4) \end{aligned}$$

The quantity, $v = V_m + KV_s$, is the effective plate volume. The fraction, $q = 1 - p$ stays in the plate. The probability P_{kn} of finding a solute molecule in the gas phase after n operations (trials) at the plate number k (the $(K + 1)$th. plate) is

$$\begin{aligned} P_{kn} &= \binom{n}{k} p^k q^{n-k} \\ &= b(k, n, p) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5) \end{aligned}$$

where $0 \leqslant k \leqslant n$. This means that as a result of n trials the solute fraction had k successes and moved to the plate number k. The expansion of the above gives the fraction of the solute in different stages. After n operations, the mean location, *i.e.* the location of the largest number of molecules on the column in terms of plate units, is given by

$$\mu = np \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

At each operation, a volume V_m of the gaseous phase is introduced into the column, so the volume throughput at the peak emergence is given by

$$\begin{aligned} \mu_v &= n V_m \; (= \dot{V_R} \text{ in Martin's equation}^3) \\ &= nvp \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7) \end{aligned}$$

If the volumetric flow rate is F per unit time, then the peak emergence time is given by

$$\mu_t = \frac{nV_m}{F} \text{ units of time}$$

$$= \frac{nvp}{F} = R_t \qquad (8)$$

Thus the statement made earlier, $R_T = f(n, v, p, F)$, is correct. In binominal distribution, the mean, that is the value of greatest probability, and the standard deviation is given by

$$\text{Mean, } \mu = np \qquad (9)$$

$$\text{Standard deviation, } \sigma = \sqrt{npq} \qquad (10)$$

When n is very large, these values can be substituted in the equation for normal distribution

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(n-\bar{n})^2/2\sigma^2}$$

and becomes

$$P_{kn} = \frac{1}{\sqrt{2\pi npq}} e^{-(k-np)^2/2npq} \qquad (11)$$

So the distribution is a continuous function of the plate number, k, corresponding to the probability of finding the largest number of fractions. This is LAPLACE's approximation.

We have already expressed the emergence time in terms of the plate number, n, the probability p, the effective plate volume, v, and the volumetric flow rate, F. Similarly, the standard deviation, σ, can be expressed in terms of the above factors. If σ_v be the standard deviation in terms of effluent volume, then

$$\sigma_v = \frac{1}{p}\sigma V_m = v\sqrt{npq} \qquad (12)$$

because the solute in the mobile phase travels $1/p$ times faster than in the stationary phase. In units of time

$$\sigma_t = \frac{v\sqrt{npq}}{F} \text{ units of time} \qquad (13)$$

Letting $p \to 0$, $q \to 1$, and $n \to \infty$ whereas $np =$ constant and is of moderate magnitude, the equation (5) becomes a POISSON function. This situation approximates the type of mechanism operating in GLPC columns, whereas binominal distribution is true for GRAIG's machine[7]. It is quite obvious from the equations 5, 8, 11, 12 and 13 that the values of μ and σ completely define the distribution curve or the macroscopic behavior of the column. Also

$$\mu_t = f(n, p, v, F) \qquad (cf.\ \text{eqn. } 8) \qquad (14)$$

and

$$\sigma_t = g(n, p, v, F) \qquad (cf.\ \text{eqn. } 13) \qquad (15)$$

Whe shall make some *a priori* assumptions here which are substantiated by our subsequent determinations. Macroscopically and microscopically, the equations 14 and 15 are true; however, the value of p and v will be affected by such microscopic effects as the film thickness, l_f, of the coating liquid, particle diameter, d_p, of the solid support, density and the nonuniformity of the packing. When a column is repacked it is hardly possible that such microscopic factors can be reproduced. Yet it is quite possible to compensate for the slight change in v and p by suitable adjustment of F. Sometimes even a slight variation in temperature accomplishes the desired effect because K and consequently p is temperature dependent. With proper adjustment of the variables it is possible to reproduce the probability and distribution of successes. Once the distribution is reproduced, the macroscopic column behavior is also reproduced.

In actual practice, one has to select a particular solute as standard (criteria for the selection of the standard are discussed later), inject it from time to time or when the column is repacked and measure the values of μ_v or μ_t and the width (a measure of σ_v or σ_t). These two parameters define the distribution curve. The adjustable variables are changed until the original values of the μ_v or μ_t and the width are reproduced. When the column behavior is thus reproduced for the standard, it is also reproduced for the other solutes. This has been verified for over a hundred compounds, for which the substrate to support ratio was varied between $\pm 5\%$. From the values of μ_t and σ_t it is possible to calculate the number of hypothetical plates of the column[8]. The number of plates required for a separation has been discussed by VAN DEEMTER *et al.*[4] and GLUECKAUF[9].

Using the same pressure differential and applying a pressure gradient correction to the apparent retention volume V_R does not insure that the same corrected retention volume $V_R^{\cdot}$ will be obtained[3,10]. Because

$$V_R^{\cdot} = fV_R = V_g^{\cdot} + KV_s \qquad \ldots\ldots\ldots\ldots\ldots (16)$$

$V_R^{\cdot}$ = corrected retention volume, f = pressure gradient correction

$$= \frac{3(P_i/P_o)^2 - 1}{2(P_i/P_o)^3 - 1}$$

V_R = apparent retention volume, $V_g^{\cdot}$ = gas hold up volume, K = partition coefficient, P_i = inlet pressure, P_o = outlet pressure.

$V_R^{\cdot}$ is an explicit function of $V_g^{\cdot}$ and KV_s. It may not be possible to reproduce $V_g^{\cdot}$ and KV_s when the column is repacked. On operating for a long time, V_s may change slightly due to evaporation from the column. The operator generally finds it necessary to change the flow rate (pressure differential) in order to obtain the same retention volumes. It has been shown earlier that the effects of slight changes of the microscopic parameters can be corrected by varying the adjustable parameters. The operator is interested in knowing that he is operating with a column of identical behavior rather than knowing the different values of $V_R^{\cdot}$ due to intrinsically changed columns.

In the foregoing discussion, the transportation of material has been assumed to be entirely due to the movement of the mobile phase. In the rate theory[4,11], the contributions of the eddy diffusion and the molecular diffusion in both the phases towards the movement of the material have also been considered. It was decided to study the contribution of the diffusional terms of the equation for the height equivalent of a theoretical plate (H) deduced by VAN DEEMTER *et al.*[4,12].

$$H = 2\lambda d_p + 2\gamma \frac{D_g}{U} + \frac{8}{\pi^2} \cdot \frac{K'Ul_f}{(1 + K')^2 D_l} \quad \ldots\ldots\ldots (17)$$

where γ = correction for the tortuosity of the channels and has a limiting value of 1, λ = a measure of packing irregularity and dependence upon particle diameter, D_g = molecular diffusion in gas phase, d_p = particle diameter, l_f = liquid film thickness, $K' = K \frac{\text{liquid phase}}{\text{gas phase}}$, U = linear velocity; D_l = molecular diffusion in liquid phase.

If one wants to calculate the value of H from this equation, a rather large number of assumption have to be made in computing the various terms of the equation which in itself is not a very desirable situation[13]. Therefore, it was decided to find experimentally the contribution of the diffusional terms under the chromatographic flow condition (flow rates > 20 ml/min). In the first series of experiments the column packing material was completely removed from the column, or in other words an empty tube was used. The tube was maintained at 80° and helium was flowing through it. Different types of solutes were introduced into the tube by momentarily stopping the helium flow. Figs. 1 to 3 show the distribution of the various solutes under a virtual coefficient of diffusivity. This type of distribution was expected from TAYLOR's study[14, 15] of the spread of the particles in a turbulent constant flow. Without going into the details of TAYLOR's calculations, a number of conclusions may be drawn from the experimental curves: (1) Under identical conditions of flow rate and temperature, distributions are more or less the same for all the compounds so far as their spread and the time of arrival at the exit of the tube are concerned. (2) At higher or chromatographic volumetric flow rates the virtual coefficient of diffusivity was negligible compared to the linear velocity. As a result there was no spread and all the solutes came out as plugs and at the same time. The time corresponded to the holding time

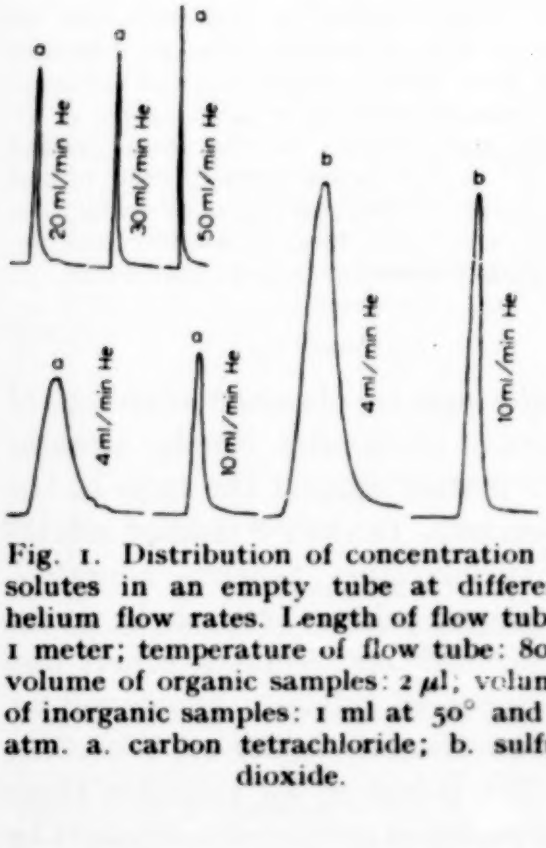

Fig. 1. Distribution of concentration of solutes in an empty tube at different helium flow rates. Length of flow tube: 1 meter; temperature of flow tube: 80°; volume of organic samples: 2 μl; volume of inorganic samples: 1 ml at 50° and 1 atm. a. carbon tetrachloride; b. sulfur dioxide.

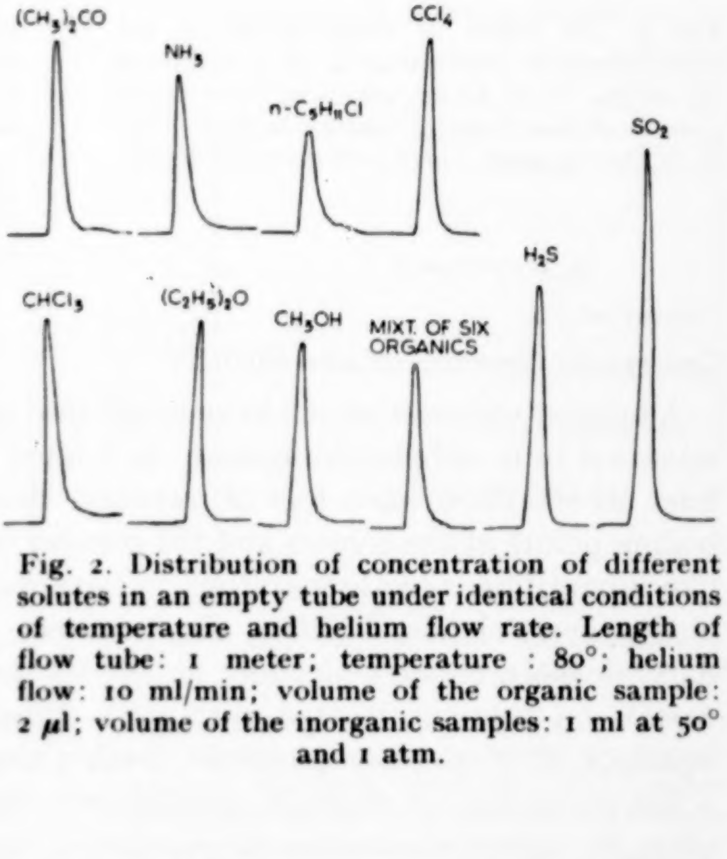

Fig. 2. Distribution of concentration of different solutes in an empty tube under identical conditions of temperature and helium flow rate. Length of flow tube: 1 meter; temperature: 80°; helium flow: 10 ml/min; volume of the organic sample: 2 μl; volume of the inorganic samples: 1 ml at 50° and 1 atm.

of the tube which depended upon the length of the tube. This means the signal was the same as that produced by a permanent gas in gas–liquid chromatography. (3) The effect of temperature is less important.

In the second series of experiments the tube was packed with sand, the distribution curves due to various solutes are shown in Fig. 4. Conclusions from these experiments are identical with those from the empty tube. Thus it appears that at the chromatographic flow rates the contribution of the first two terms of VAN DEEMTER's equation are negligible or at the most they may be substituted by a suitable constant.

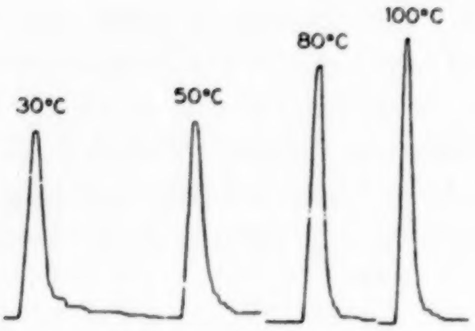

Fig. 3. The effect of temperature on the distribution of concentration of a solute in an empty tube under identical flow rates. Length of flow tube: 1 meter; helium flow: 10 ml/min; sample: 2 μl of carbon tetrachloride.

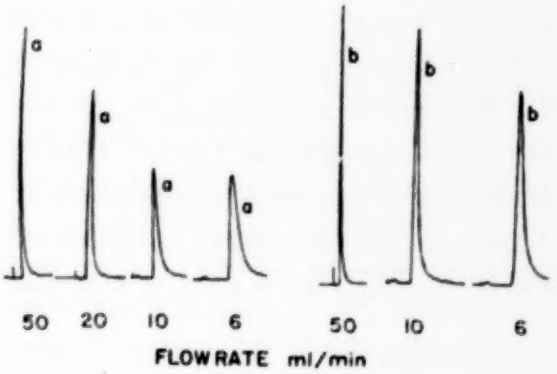

Fig. 4. Distribution of concentration of solutes in a sand packed tube at different helium flow rates. Length of sand column: 90 cm; screen fraction of sand: 40/80 mesh fraction; temperature of the sand packed tube: 80°. a. 2 μl carbon tetrachloride; b. 2 μl of a mixture of equal volumes of allyl chloride, acetone, *sec.* butyl chloride, *n*-amyl chloride, carbon tetrachloride and chloroform.

Criteria for favorable column behavior

A number of investigators have found that straight lines are obtained when logs of retention time are plotted against the boiling points of the solutes. Similar straight lines are obtained when logs of retention time are plotted against the ratio of the boiling points of the solutes and the column temperature. TENNEY[16] studied solutes like *n*-paraffins, 2-methylparaffins, cyclopentanes, cyclohexanes, 1-olefins, 2-methylolefins, cyclo-olefins, diolefins, alkylbenzenes, acetylenes, primary *n*-alcohols, secondary alcohols, tertiary alcohols, aldehydes, ketones, formates, acetates, ethers and acetals on columns treated with such different types of solvants as convoil-20, squalane, β, β'-oxydipropionitrile, 2-ethyl hexyl sebacate, convachlor-20. With only a few exceptions he obtained straight lines for boiling points *vs.* log retention times plots. Straight lines are also obtained when logs of partition coefficients obtained by chromatographic methods are plotted against the ratio of the boiling point of the solute to the column temperature (*cf.* Figs. 5 and 6). This is expected because the retention time changes linearly with partition coefficients (*cf.* eqns. 4, 7 and 8). It was expected and also found that similar straight line plots are obtained when the latent heats of vaporization are plotted against logs of partition coefficients (*cf.* Figs. 7 and 8). The above conclusions are true only for the compounds of the same family. Cyclopentane, being a compound of another family, did not fall in the straight line (*cf.* Figs. 5–8). It is also interesting to note that column temperature higher than the critical temperature of the solutes were never used.

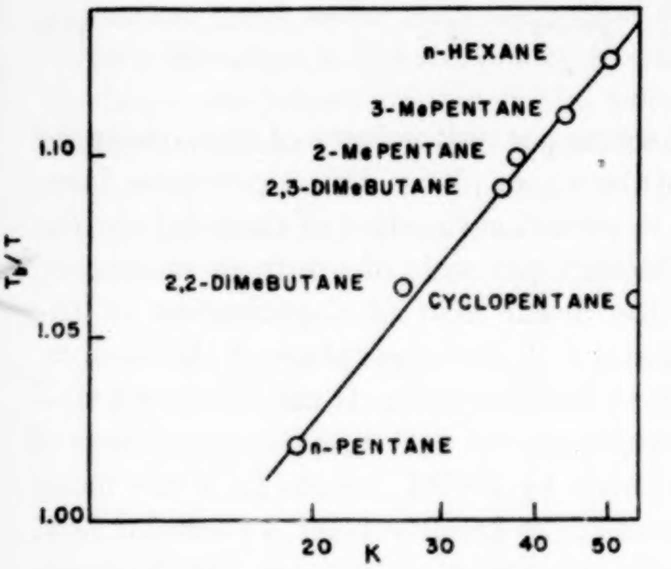

Fig. 5. Change of log partition coefficient with the ratio of boiling point to column temperature. T_b(°K) = b.p.; T(°K) = col. temp. Data taken from KEULEMANS[12]. Column: Dimethylsulfolane. Note: Cyclopentane did not fall in line with the chain hydrocarbon.

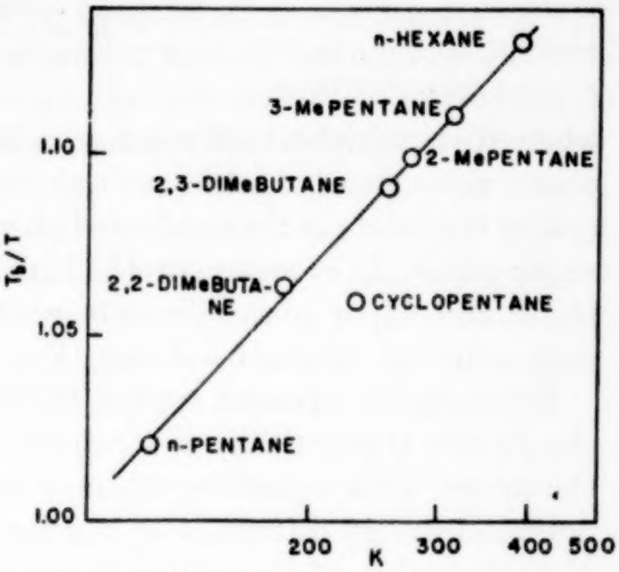

Fig. 6. Change of log partition coefficient with the ratio of boiling point to column temperature. T_b(°K) = b.p.; T(°K) = col. temp. Column: n-Hexadecane. Data taken from KEULEMANS[12]. Note: In this case cyclopentane is closer to the line because of the low polarity of the substrate.

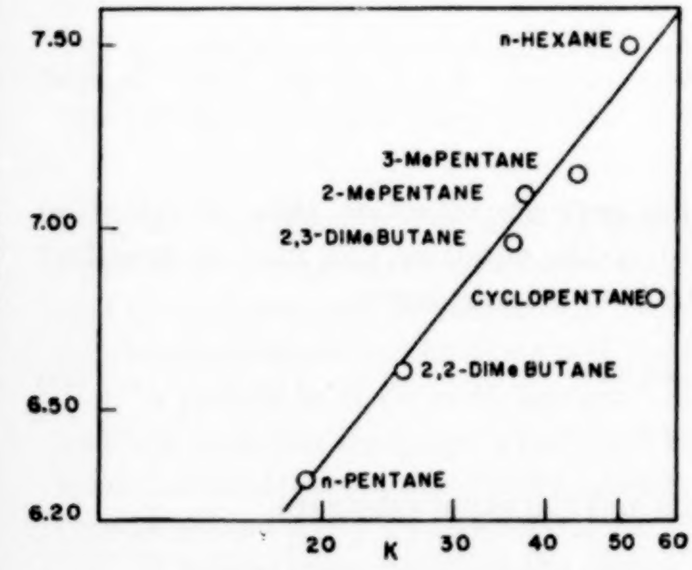

Fig. 7. Change of log partition coefficient with the molar heat of vaporization at constant pressure. Partition coefficient data taken from KEULEMANS[12] and heat of vaporization (at 25°) data taken from Chemical Engineers' Handbook. Column: Dimethylsulfolane.

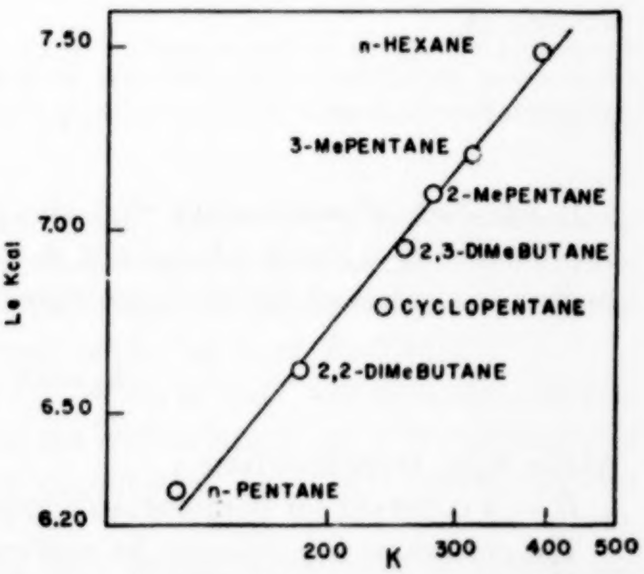

Fig. 8. Change of log partition coefficient with the molar heat of vaporization at constant pressure. Partition coefficient data taken from KEULEMANS[12] and heat of vaporization (at 25°) data taken from Chemical Engineers' Handbook. Column: n-Hexadecane.

Examination of data obtained by TENNEY[16] reveals yet another interesting feature (*cf.* Fig. 2 of ref.[16]). The intercept of the log retention time *vs.* boiling point curve is practically independent of temperature even for a temperature differential of 50°. The temperature coefficient of the slope is also very small. These results are expected from the general equation for the distribution coefficient in a two component–two phase assembly[17].

$$K = \frac{n_l}{n_v} = \frac{Pf_l}{Pf_v} \cdot e^{Li/RT} \qquad (18)$$

where K = partition coefficient, n_l = moles of solute per unit volume of the condensed phase, n_v = moles of solute per unit volume of the vapor phase, Pf_l = partition function of the solute in the condensed phase, Pf_v = partition function of the solute in the vapor phase, Li = mean potential energy difference per mole of solute in condensed phase and vapor phase (linearly related to the molar heat of vaporization of the pure solute at constant volume), R = gas constant, T = temperature of the system.

For an one component system Pf_l/Pf_v tends to become unity. It can be shown that the Pf_l/Pf_v is practically independent of temperature for very low concentrations of the solute. Li in equation (18) may be substituted by Le/RT, where Le is the mean potential energy difference at constant pressure (Le is linearly related to molar heat of vaporization of the solute at constant pressure) and the equation (18) becomes

$$\begin{aligned} K &= A' e^{(Le/RT)-1} \\ &= A e^{Le/RT} \qquad (19) \end{aligned}$$

Because the plot of log K against T_b/T (T_b = boiling point in °K) produces straight lines (*cf.* Figs. 5 and 6), it may be expected that a relation similar to TROUTON's rule exists between T_b and Le in the case of dilute solutions and the equation (19) may be written as

$$K = A\, e^{\alpha T_b/RT} \qquad (20)$$

where

$$Le/T_b = \alpha$$

It has been shown earlier that the relation between retention time or retention volume and K is linear (*cf.* eqns. 7, 8, and 16), so the equation (20) may be modified to give an expression for retention time or retention volume, hence

$$R_t = fK = Be^{\alpha T_b/RT} \qquad (21)$$

where R_t = retention time

B = a constant for homologous compounds and the same substrate

The equations (19–21) may be written as

$$\ln K = \ln A + Le/RT \qquad (22)$$

$$\ln K = \ln A + \alpha\, T_b/RT \qquad (23)$$

$$\ln R_t = \ln B + \alpha\, T_b/RT \qquad (24)$$

We can draw a number of conclusions from the equations (19–24).

1. The partition coefficient or the retention time will change expontentially with the change of the ratio Le/T or T_b/T. It is expected that for T_b/T ratio higher than unity R_t will increase very rapidly. Fig. 9 illustrates a plot n_l/n_v against T_b/T assuming $A = 1$ and $\alpha = 23$ (one component two phase system). At lower T_b/T ratios (when $T \geqslant$ critical temperature), n_l/n_v will be constant at constant pressure and the above relations are not strictly applicable. In other words, it may be safely concluded that at column tem-

peratures much lower than the boiling point of the solute ($T_b/T \gg 1$) most of the molecules will remain in the stationary (condensed) phase for most of the time and there will be fewer exchanges between the two phases, *i.e.* the column will be inefficient. At column temperatures much higher than the boiling point of the solute (say $T_b/T \leqslant 0.6$; for pure compounds the ratio of boiling and critical temperature is approximately equal to 0.6) most of the molecules will remain in the vapor phase for most of the time and the column will be inefficient. However, the actual optimum temperature range will be determined by the slope and the intercept of the log R_t *vs.* T_b/T plot.

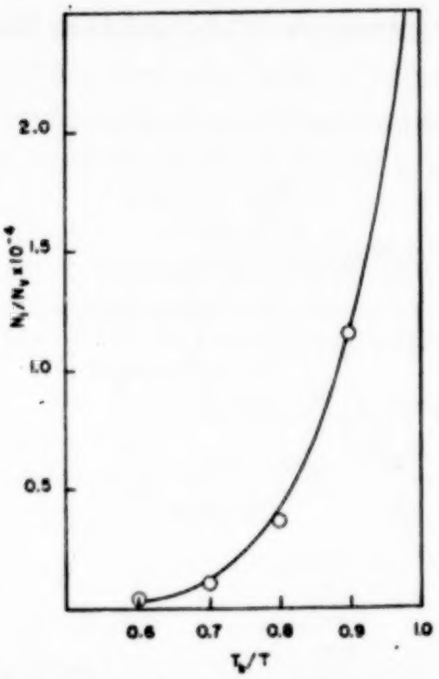

Fig. 9. Change of the ratio of number moles/unit volume of the liquid to number of moles/unit volume of the vapor in equilibrium at temperature T°K with the ratio of the boiling point to the equilibrium temperature. T_b = b.p.(°K); T = equilibrium temperature = column temperature (°K).

2. A plot of ln K or ln R_t against Le, or Le/T, or T_b or T_b/T will be a straight line and will make an intercept which will be constant and independent of temperature at least for moderate temperature ranges. This expectation has been verified by our results as well as by TENNEY's[16] data.

3. It is also expected that the slopes of the plots for different types of compounds will not be very different (*cf.* Figs. 5–8 and TENNEY[16]).

4. Combination of equations (7) and (16) and (23) should enable us to determine K and its temperature dependence in a very straight-forward manner.

Recommendation for determining the optimum column conditions

The choice of temperature of the column is the first parameter to be decided. It should be realized from the preceding discussion that any one column temperature cannot be suitable for all the solutes. The column temperature will be determined by the boiling point of the lowest boiling solute in a mixture. The optimum column temperature is given by a value of the T_b/T ratio between 1 and 0.92. The compounds boiling between the column temperature and 0.92 times the column temperature will be very nicely resolved. (*cf.* Fig. 10).

After the column temperature has been fixed, a standard solute is selected, boiling as close possible to the column temperature, preferably slightly below the column temperature. This compound should not be highly polar and should have normal heat of vaporization ($Le/T_b \approx 23$). A volume of this solute, less than the plate volume, should be injected into the column at different flow rates until the flow rate corresponding to the maximum number of plates is obtained. The optimum temperature and the flow rate are thus determined. The condition of the column can be checked

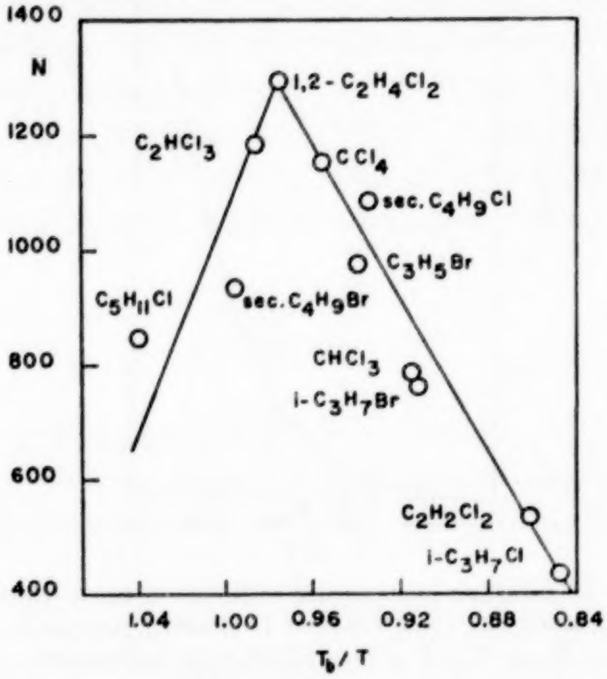

Fig. 10. Variation of the number of plates with boiling point of the solutes. Column: 20% tri-*m*-tolyl phosphate on 30/60 celite; column length: 2 meter; column temperature: 93°; He flow rates: 52 ml/min. Widely varying types of halogenated hydrocarbons were deliberately chosen to emphasize the importance of the boiling point, even when the compounds do not strictly belong to the same family.

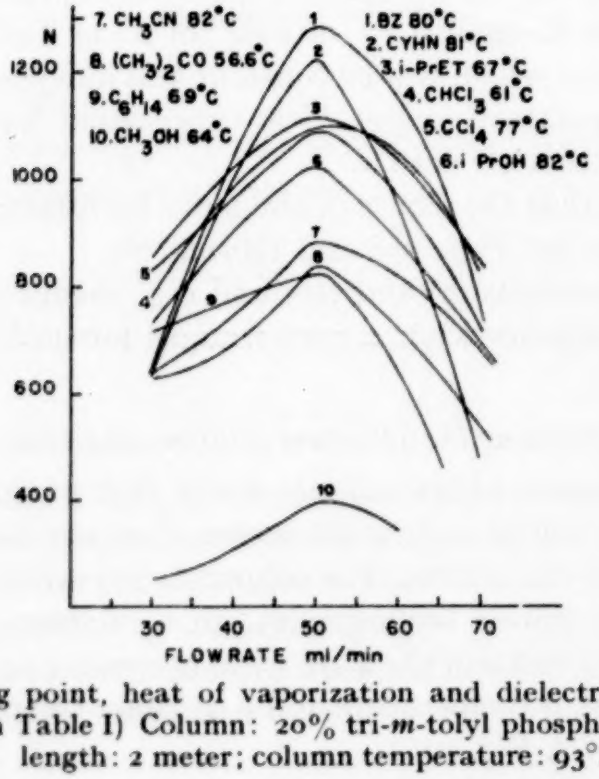

Fig. 11. Effect of boiling point, heat of vaporization and dielectric constant on the column efficiency. (Compare with Table I) Column: 20% tri-*m*-tolyl phosphate on 30/60 celite; column length: 2 meter; column temperature: 93°.

every now and then by injecting the standard, and the overall column behavior maintained uniform by adjusting the flow rate and, very rarely, the temperature. The reason that a solute having a boiling point near the column temperature is selected is that the slightest change in column condition is reflected in the number of plates. When the column is repacked with the same material, the same plate number is reproduced by adjusting the flow rate and the column temperature. The retention times may be easily expressed in terms of the standard. It was also found that for the same column, optimum flow rate was the same irrespective of T_b/T ratio, although the absolute efficiency of the column was different depending on the value of T_b/T ratio, the dielectric constant and the heat of vaporization (*cf.* Fig. 11 and Table I).

TABLE I

EFFECT OF BOILING POINT, HEAT OF VAPORIZATION, AND DIELECTRIC CONSTANT ON COLUMN EFFICIENCY

(Compare with plate number in Fig. 11)

Column: 20% tri-*m*-tolyl phosphate on 30/60 celite; column length: 2 meter; column temperature: 93°.

Solute	*b.p. (T°K) to col. temp. (T°K) ratio*	*Mol. heat of vapor const P and at b.p. K cal.*	*Dielectric constant at 20°*
Acetonitrite (7)	0.97	7.15	38.8
Isopropyl alcohol (6)	0.97	9.55	18.9
Cyclohexane (2)	0.97	6.95	2.0
Benzene (1)	0.965	7.3	2.3
Carbon tetrachloride (5)	0.955	7.1	2.2
n-Hexane (9)	0.935	6.95	1.9
Isopropyl ether (3)	0.93	—	—
Methanol (10)	0.915	8.4	32.6
Chloroform (4)	0.915	7.05	4.4
Acetone (8)	0.90	7.2	21.4

ACKNOWLEDGEMENT

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SUMMARY

The distribution of a solute in a gas–liquid chromatographic column has been discussed from the probability view point and its analogy to the Bernoulli trial system has been shown. It has been shown that the reproduction of column behavior is possible by reproducing the probability. The criterion for the optimum column temperature has also been discussed. Recommendations have been made for determining the optimum column conditions and its reproduction.

RÉSUMÉ

L'auteur a effectué une étude, à l'aide du calcul des probabilités, sur le comportement d'une substance dans une colonne chromatographique gaz–liquide. On a déterminé également les conditions optimales et la reproductibilité.

ZUSAMMENFASSUNG

Es wurde versucht, die Bewegung und Verteilung einer Substanz in einer gas–flüssig Chromatographie-Kolonne mit Hilfe der Wahrscheinlichkeitsrechnung zu erklären. Die Kriterien für die optimale Kolonnentemperatur werden diskutiert und Vorschläge gemacht zur Bestimmung der optimalen Kolonnen-Bedingungen und deren Reproduzierbarkeit.

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CHROMATOGRAPHIC SEPARATION OF SOME ALKALI METALS

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Numerous papers have been published[1–8] on the separation of the group I metals possibly none more successful than that of Linstead[1], all however, suffer from the difficulty of identifying the position of the metal ions after development. As these metals travel as ions it occurred to the author that a combination of Linstead methanol solvent to which some aqueous ammonia was added and using an acid base indicator as detector would prove simple and effective. This proved to be the case.

EXPERIMENTAL

The solvent

Pure methanol was used in early trials but redistilled commercial methanol proved successful in later experiments. To this was added one to ten percent of 15 *N* aqueous ammonia. Solvents based on ethanol *n*-proponal and *n*-butanol were used with less success.

The chromatograms

These were made by the ascending techniques using Whatman's No. 1 paper cut into sheets 20 cm by 28 cm. The spots of solution containing the alkali metal were placed on a line 3 cm from one of the longer edges and with a distance of 2.5 cm between spots. The spots nearest the vertical edges of the paper were at least 6 cm from it. The paper was coiled into a cylinder and sewn with cotton at top and bottom. This served to keep the cylinder rigid. The spots were placed on the paper with a platinum loop which held about 0.005 ml of solution, and were air dried before placing in the development jar. This latter was a 3-l Winchester jar from which the neck had been cut and the edge ground flat. The vessel was closed with a 15-cm square of plate glass. An 11-cm Petri dish carrying the solvent was placed in the bottom of the development jar and the cylinder of paper was lowered into it. No humidification period was given the paper. The time of development varied a little but none was greater than 90 min at 20 to 25° for a height of about 18 cm from the surface of the solvent pool.

Identification of the spots was obtained by spraying the partially dried paper with a 0.005 % solution of bromophenol blue in 20% alcohol which had been neutralized with 0.1 N NaOH solution. The paper was then treated for 15 to 30 min in an oven at 100°. The alkali spots appeared purple against a ground of yellow where the acid ions were purplish grey on most of the paper. The spots were quite easily distinguishable over the usual tenfold range of concentration used in paper chromatography.

Metal ion solution

The alkali metals, magnesium, calcium, strontium, barium, silver, cadmium were used as chlorides or nitrates at concentrations of 0.1 M in metal ion. When the effect of the anion was being studied, lithium, sodium or potassium were tried as sulphate, perchlorate, bromide, iodide and carbonate.

R_F values of metal ions

The R_F values of the ions were measured relative to the liquid front, no adsorption front being obtained with methanol although some of the other alcohol solutions gave one. The following results refer to nitrate solutions. The R_F values obtained for methanol with 1% and 5% of 15 N ammonia are the only ones given. A solution with ½% ammonia did not give satisfactory results. R_F values for concentrations over 5% had no advantages. A 2% solution gave values slightly greater than the 5% solution.

Metal ion:	*Li*	*Na*	*K*	*Rb*	*Cs*	*Mg*	*Ca*	*Sr*	*Ba*	*Ag*	*Cd*
1% 15 N NH_3	0.82	0.40	0.19	0.16	0.16	0	0.75*	0.75*	0.33*	0.38	0.35
5% 15 N NH_3	0.74	0.30	0.12	0.12	0.10	0	0.4*	0.4*	0.3*	—	—

Those values marked with an asterisk trailed from the base to the value indicated. The results for solutions containing anions other than nitrate showed no significant variation where the anion was monovalent. However, carbonate and sulphate gave considerably lower values for lithium, sodium and potassium at 0.7, 0.3 and 0.1 respectively.

DISCUSSION

As was found by LINSTEAD, methanol proved to be the best solvent to obtain separation of the ions. A butanol–water–ammonia mixture gave higher R_F values for potassium, rubidium and caesium, but no separation, and thus was of no value. Indicator solutions other than bromophenol blue were tried but were no more successful.

In theory, any indicator with a pK value of the same order as bromophenol blue should be satisfactory.

As would be expected, the position of the acid ion was revealed as a yellow spot. This usually trailed over a considerable distance and did not noticeably interfere with the cation spot. It did indicate, however, that the cation travelled independently of the anion with which it was associated. This point is borne out by radiographic identification of spots from salts in which both anion and cation are radioactive.

The alkaline earth metals from spots which are nearer the neutral colour of bromophenol blue and which trail, except magnesium which does not move, from the base line to the height indicated above. It seems that they are precipitated as carbonates during the course of the chromatogram. Silver and cadmium as the ammines give clear cut oval spots of hue similar to the alkali metal spots.

The method gives a simple means of identifying the alkali metal salts after a preliminary sulphide or basic carbonate separation of other metals and conversion to chloride or nitrate solution. Its possibilities as a means of gravimetric determination of lithium, sodium and potassium are being investigated.

SUMMARY

The chromatography of the alkali metals is described using 5% 15 *N* NH_3 in methanol as solvent and bromophenol blue to identify the spots. Interfering elements have been studied. The method gives a rapid and more positive method of separation and identification than previously possible.

RÉSUMÉ

Une séparation chromatographique des métaux alcalins est décrite. On utilise du méthanol, renfermant 5% d'ammoniaque 15 *N*, comme solvant et le bleu de bromophénol pour identifier les spots. Cette méthode est simple et rapide.

ZUSAMMENFASSUNG

Es wird eine chromatographische Trennungsmethode für die Alkalimetalle beschrieben. Als Lösungsmittel wird Methanol mit einem Zusatz von 5% 15 *N* Ammoniak verwendet. Die Identifizierung der Flecken erfolgt mit Bromphenolblau. Die Methode ist einfach und rasch.

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Anal. Chim. Acta, 22 (1960) 142–144

THE SPECTROCHEMICAL DETERMINATION OF TOTAL STRONTIUM IN BONE, MILK AND VEGETATION

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INTRODUCTION

In recent years the physiological effects produced by radioactive fission products from atomic weapons have necessitated an intensified study of the metabolism of strontium in animals and plants. The spectrographic methods outlined below were developed in response to a demand for the rapid and economic determination of total strontium in samples of ash obtained from bone, milk and vegetation.

PRELIMINARY

The spectrographic examination of bone ash was comparatively straightforward because the composition of the bone ash did not vary in its major constituents and this facilitated standardisation, but the presence of large amounts of alkali metals in the ash of milk and vegetation and the variable composition of the latter made the application of direct spectrographic methods doubtful.

In the normal course of events the calcium is determined chemically as part of the analytical scheme and it was relatively easy to modify the procedure to make the calcium and strontium oxalate precipitate available for the spectrographic analysis.

Examination of bone ash

A number of workers have examined the mineral content of bones[1-7] but their references to strontium were largely of qualitative significance. More recently quantitative estimation of strontium in bones has been carried out by emission spectroscopy[8,9] and by the neutron activation technique[10].

The spectrographic method of HODGES *et al.*[8], in which an admixture of the sample with graphite and copper sulphate is excited in a d.c.-arc, appeared to be capable of modification to permit the determination of strontium in strontium and calcium oxalate fractions separated from milk and vegetation ash. This method had one disadvantage, however, in that the coefficient of variation of 10% for a mean of triplicate exposures was inadequate and experiments were carried out with a view to improving the precision of the method.

The feasibility of using additional internal standards apart from copper was examined, calcium and barium being tried but without any improvement being obtained. Eventually improved arc stability was obtained by using a larger proportion of graphite and substituting anhydrous copper sulphate for the pentahydrate, the admixture of sample with graphite and anhydrous copper sulphate being pelleted before burning in the arc. These modifications, combined with the microphotometry of a different copper line (at 4704.6 Å) from that advocated by HODGES *et al.*, gave an improved coefficient of variation of 6% for single exposures (3.5% for the mean of triplicate exposures) at the 90 p.p.m. level.

A calibration curve (Fig. 4) was obtained from standards made by grinding strontium carbonate into calcium phosphate. The calcium phosphate used for these standards was made from calcium carbonate which had been freed from strontium by the fractional precipitation of their compounds with 8-hydroxyquinoline[11,12].

Method (bone ash)

Copper sulphate and graphite powder are added to the bone ash in known proportions. Pellets prepared from this mixture are burnt to completion in graphite cups at 7 A d.c. Spectra are evaluated by non-recording microphotometry, calibration being carried out by means of an iron intensity pattern.

The strontium content is determined by comparison with standards made by mixing strontium carbonate with calcium phosphate in known proportions.

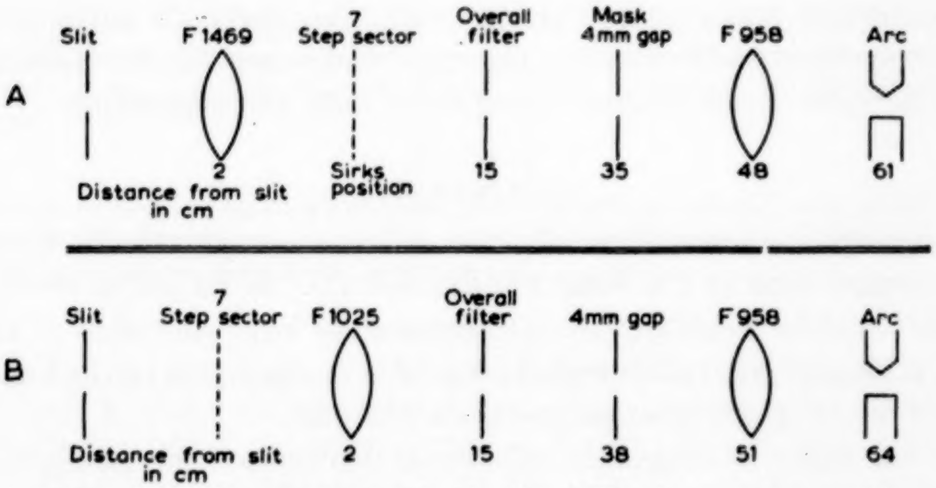
A
Slit
F 1469
7 Step sector
Overall filter
Mask 4mm gap
F 958
Arc
2
Sirks position
15
35
48
61
Distance from slit in cm
B
Slit
7 Step sector
F 1025
Overall filter
4mm gap
F958
Arc
Distance from slit in cm
2
15
38
51
64

Fig. 1. Optics external to the spectrograph. A. For Hilger's 3-metre grating spectrograph. B. For large automatic quartz spectrograph.

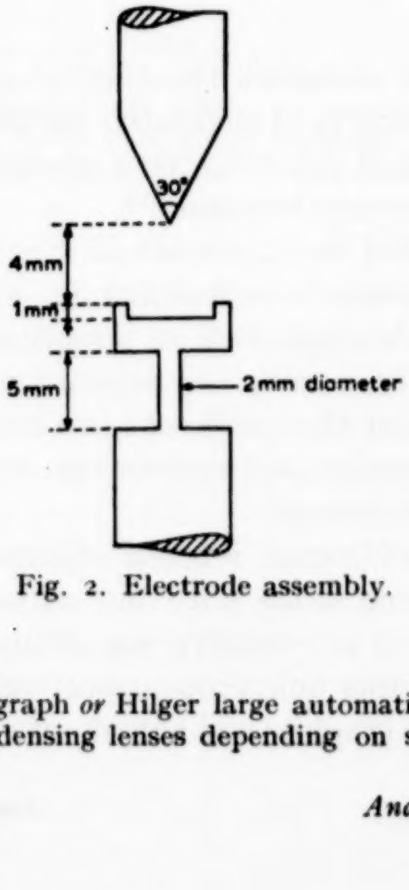
30°
4mm
1mm
5mm
2mm diameter

Fig. 2. Electrode assembly.

Special apparatus

Hilger 3-metre grating spectrograph *or* Hilger large automatic quartz spectrograph; de Gramont Arc and Spark stand, condensing lenses depending on spectrograph used (see Fig. 1);

Sighting lamp and screen/mask; Quartz filter (20% transmission); N.C.C. graphite electrodes 1/4″ diameter; Matthey 7-mm diameter copper electrodes; Matthey 5-mm diameter iron electrodes; Non-recording microphotometer; Hilger rotating 7-step sector.

Spectrographic conditions

Spectrograph	Hilger 3-metre grating	Hilger large automatic quartz
External optics	See Fig. 1(a)	See Fig. 1(b)
Plate mask	1.8 mm	3 mm
Slit length	20 mm	1.8 mm
Slit width	0.015 mm	
Wavelength range	3500–5000 Å(1st order)	3200–8000 Å
Optical filters	Overall neutral quartz filter 20% transmission	
Photographic plate	Ilford Ordinary	
Top electrode (—ve)	1/4″ diameter N.C.C. graphite 30° cone	
Bottom electrode (+ve)	1/4″ diameter N.C.C. graphite specially machined (See Fig. 2)	
Analytical gap	4 mm	
Sample load	Pellets prepared in special block (see Fig. 3)	
Current	7 A d.c.	
Exposure	Complete burn (indicated by the arc becoming unstable and noisy)	

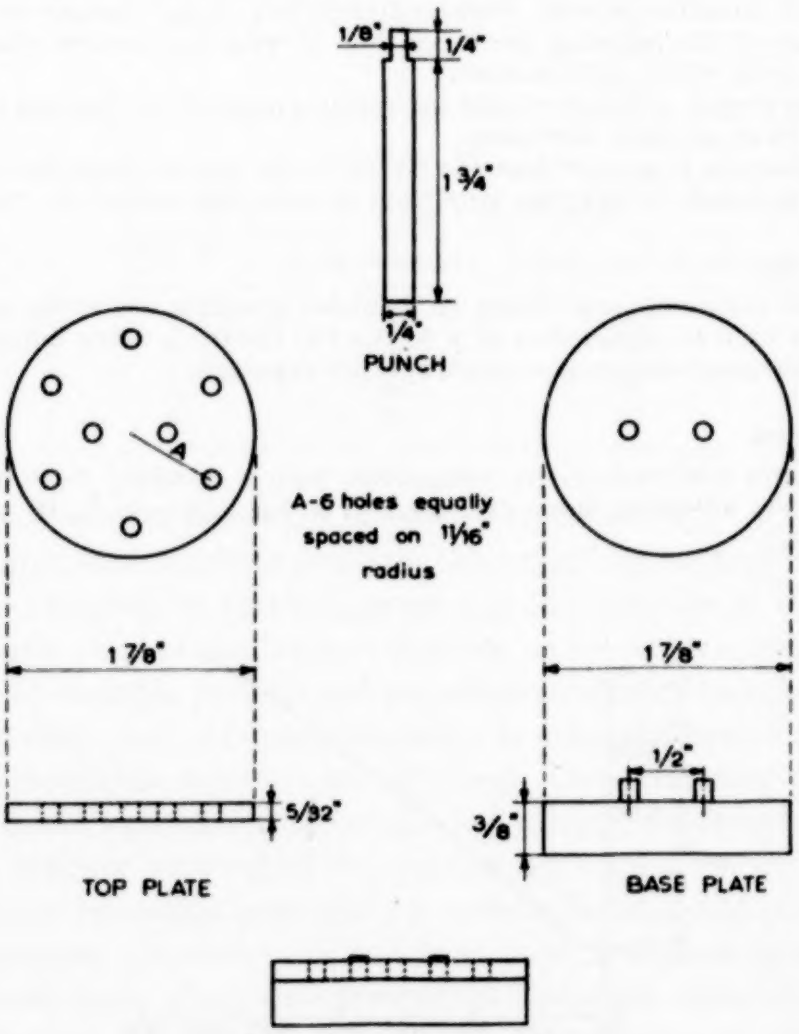

Fig. 3. Pelleting block.

Plate calibration spectrum

After completing exposure of samples or standards, photograph on the same plate an intensity pattern by means of the 7-step rotating sector (step ratio 1 : 2).

Spectrograph	Hilger 3-metre grating	Hilger large automatic quartz
Position of sector	At Sirks position	At slit
Top electrode (+ve)	Matthey 7 mm copper, 80° cone	
Bottom electrode (—ve)	Matthey 5 mm iron, flat	

Slit length	20 mm	12 mm
Plate mask	12 mm	
Analytical gap	3 mm	
Current	3.4 A d.c.	
Pre-arc	30 sec	
Exposure	25 sec	

Photographic processing

Develop in I D.2 for 4 min at 20°.

Rinse with water and fix in acid hypo until the plate is completely clear.

Wash for half an hour in an efficient washing tank and allow to dry.

Drying may be accelerated by soaking the plate in 80% methylated spirits for 2 min.

Standards

Prepare by dry grinding in an agate mortar a mixture of strontium carbonate and strontium-free calcium phosphate such that the final matrix contains 1,000 p.p.m. of strontium. By further dilution prepare standards containing 400, 300, 250, 200, 150, 100 and 50 p.p.m.

Preparation of sample

Grind in an agate mortar for five min 15 mg of sample with 135 mg of anhydrous copper sulphate and 150 mg of N.C.C. graphite powder. Prepare five pellets of each sample by loosely filling the holes in the die-plate of the pelleting block (see Fig. 3) with the powder, placing the punch in position and giving a tap with a light hammer.

Note: the anhydrous copper sulphate should be freshly prepared, by heating to constant weight at 250°, and stored in an air tight container.

If the strontium content is greater than 350 p.p.m. in the matrix dilute the sample with strontium-free calcium phosphate so that the strontium content falls within the range 50–350 p.p.m.

Spectrographic procedure

Place a pellet into the anode cup. Using an insulated graphite rod strike an arc between the electrodes. Allow to burn to completion at 7 A, the top electrode being adjusted to maintain a constant gap. Repeat three times to give quadruplicate exposures.

Interpretation of spectra

Examine the spectra qualitatively by comparison with a standard plate in a comparator to identify and mark the following lines: Sr I 4607.33 Å, Cu I 4704.59 Å, Fe 4678.85 Å (in plate calibration spectrum).

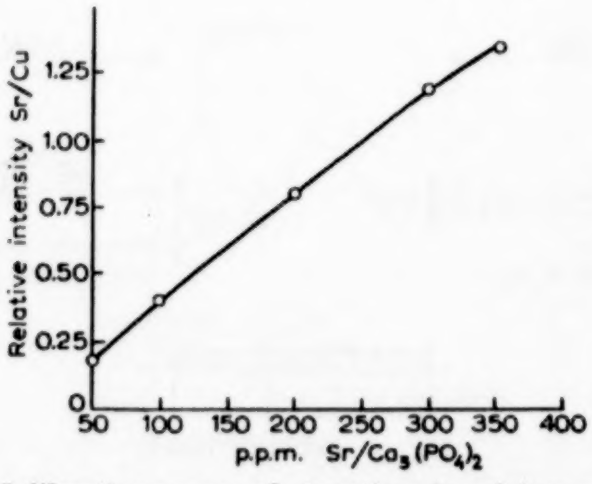

Fig. 4. Calibration curve, of strontium in calcium phosphate.

Measure the Seidel densities of the strontium and copper lines and of the iron line in the steps of the plate calibration spectrum.

Plot a curve of Seidel density of sectored iron line against log relative intensity (from the known step-ratios). By means of the curve obtained, convert Seidel densities of strontium and copper to log relative intensities, and so obtain intensity ratios of strontium/copper. Read the final concentration of strontium from the appropriate calibration curve.

Standardisation (Preparation of calibration curves)

Calibration curves are prepared as above from standards made by dry grinding of strontium carbonate with strontium-free calcium phosphate, plotting the relative intensity of the strontium line divided by the relative intensity of the copper line against the concentration of strontium (see Fig. 4).

ACCURACY AND PRECISION

The precision of the method was determined by the replication on three photographic plates of a sample of bone ash known to contain 90 p.p.m. of strontium. The coefficient of variation was 6 % for single exposures.

As a check on the accuracy, samples were examined by the neutron activation and X-ray fluorescence techniques and no significant bias was evident, as will be seen from Tables I and II below.

TABLE I

Bone ash sample No.	*p.p.m. strontium in ash*	
	Neutron activation	*Emission spectroscopy*
1	86	85
2	98	100
3	114	110
4	118	120

TABLE II

Bone ash sample No.	*p.p.m. strontium in ash*	
	X-ray fluorescence	*Emission spectroscopy*
5	134	135
6	90	90
7	198	190
8	80	80

Examination of milk ash and vegetation (Emission spectroscopy)

Initially, attempts were made to evaluate the strontium content of milk and vegetation ash by spectrographic methods involving the dilution of the sample with a large excess of ferric sulphate or barium chloride as spectrographic buffer[13-15]. The relatively high and variable sodium and potassium contents together with the presence of chloride, silica and phosphate resulted in a breakdown of the buffer effect, and erratic and unreliable results were obtained. Unsatisfactory results were also obtained by the direct application of the method already described for bone ash, for a similar reason. Neither removal of the chloride by sulphation nor admixture with salts of metals of low ionisation potential *e.g.* sodium fluoride and potassium sulphate gave any improvement. Lithium salts had been used as a spectrographic buffer and flux for the determination of various elements in biological materials[16,17], but its use in this connection was precluded owing to the interference of the most sensitive strontium line by diffuse lithium lines.

It was therefore concluded that the evolution of a direct spectrographic method appropriate to both milk ash and a wide range of vegetation ashes might necessitate a protracted investigational programme. Efforts were directed accordingly to the separation of strontium from the interfering elements and this was accomplished by precipitation of the oxalates at pH 4.0 and a temperature of 0° after removal of any siliceous matter[18].

A modification of the method used for the determination of strontium in bone ash was then applied to the determination of strontium in calcium–strontium oxalate (monohydrate) fractions separated from the ashes of milk and vegetation.

The mixed oxalate fractions were ground with graphite and anhydrous copper sulphate and the spectra recorded and assessed by the method already described for the determination of strontium in bone ash, a calibration curve (Fig. 5) being constructed from standards prepared by the grinding of strontium carbonate into calcium oxalate monohydrate.

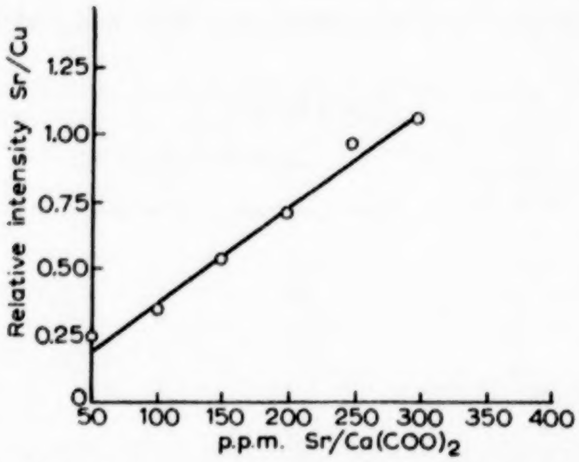

Fig. 5. Calibration curve of strontium in calcium oxalate.

Examination of milk ash and vegetation ash (flame photometry)

Once strontium could be separated easily from interfering elements flame photometry became an attractive possibility. The essential requirement was a flame photometer of adequate sensitivity, resolution and stability combined with a high flame temperature. In view of the heavy background produced an automatic background correction was considered desirable for the attainment of adequate sensitivity.

In the instrument designed and constructed at Woolwich[19] the features outlined above are incorporated, together with an integrating device; an oxy–propane flame is used with direct oxygen atomisation of the sample into the flame. A filtered air jacket is also incorporated to prevent atmospheric contamination and to smooth the edges of the flame, thus contributing to stability of the system. With this instrument 0.1 p.p.m. of strontium can be determined in the presence of 1000 p.p.m. of calcium with a precision of better than 5% per determination.

Standard solutions were made up by dissolving the appropriate amounts of strontium carbonate, calcium carbonate and oxalic acid in the minimum quantity of hydrochloric acid and the strontium/calcium ratios of the solution of the sample determined.

Reagents

Hydrochloric acid, conc., $d = 1.16$, calcium carbonate, strontium free, and dried at 100°, strontium carbonate, dried at 100° and oxalic acid.

Whenever possible all reagents should be of "AnalaR" quality and the use of redistilled or demineralized water is implied throughout.

Standards

(1) *Master solution of strontium, 1000 p.p.m.* Weigh out 0.169 g of strontium carbonate into a beaker. Cover with 10–20 ml of redistilled water and add conc. hydrochloric acid dropwise

until dissolved. Make up to 100 ml with water to give a master solution containing 1000 p.p.m. of strontium in solution. Dilute this master solution as necessary to give working standard solutions.

This solution should be bottled in polythene which has previously had prolonged washing with redistilled water.

(2) *Master solution of calcium chloride 1/8 M.* Weigh out 2.497 g of calcium carbonate and dissolve in just sufficient concentrated hydrochloric acid (about 4 ml) and 10 ml of water. Make up to 200 ml with redistilled water.

(3) *Oxalic acid solution 1/8 M.* Weigh out 3.150 g of oxalic acid ($(COOH)_2 \cdot 2H_2O$) and make up to 200 ml with redistilled water.

(4) *"Blank" solution.* Measure out 10 ml of the master solution of calcium and transfer to a 50-ml flask. Add to this 2.5 ml of conc. hydrochloric acid and 10 ml of the oxalic acid solution. Make up to 50 ml with redistilled water.

(5) *Standard for milk.* Proceed as in (4) above but before making up to 50 ml, add 5 ml of 10 p.p.m. strontium solution (prepared from successive dilution of the master solution). This gives a standard containing 1000 p.p.m. of strontium with respect to calcium.

(6) *Standard for vegetation.* Proceed as in (5) above but add 5 ml of 100 p.p.m. strontium solution. This gives a standard containing 10,000 p.p.m. of strontium with respect to calcium.

PROCEDURE

Preparation of sample

Dissolve 36.5 mg of the sample in the form of calcium oxalate monohydrate in 0.5 ml of conc. hydrochloric acid and 1 ml of redistilled water (warm if necessary). Allow to cool and make up to 10 ml with redistilled water.

Flame photometry

Switch on the instrument and allow 30 min to warm up. Light the burner and adjust if necessary for optimum atomisation. Set the internal standard gain control to give an integration time of 10–15 sec with 0.1% calcium oxalate solution. A full description of the instrument with directions for use is given in AERE C/R. 2659 (in course of publication). Adjust the gain on the line and background channels to give full scale deflection for the top standard.

Note: The top standard will contain 1 p.p.m. of strontium for milk or 10 p.p.m. for vegetation. Set the zero control for the blank solution. Repeat as necessary.

Note: The zero and gain controls are not entirely independent *i.e.* resetting of one may affect the other so that repeated adjustments may be necessary.

Obtain the readings for each sample in turn, re-calibrating as necessary.

Note: Since linear calibration is obtained in the case of the Woolwich instrument the strontium content may be read directly from the dial reading.

PRECISION AND ACCURACY (MILK ASH AND VEGETATION ASH)

The accuracy of the method was assessed by comparison between the techniques of neutron activation, X-ray fluorescence, emission spectroscopy and flame photometry, and the results are given in Table III. The coefficient of variation of the whole analytical operation (including flame photometry) is 5% per determination.

TABLE III

All results expressed as p.p.m. strontium in milk ash

Sample No.	*Flame photometry*	*Emission spectroscopy*	*Neutron activation*	*X-ray fluorescence*
M969	33	31	32	34
M971	64	64	63	65
M972	51	45	53	56
M973	41	38	39	45
M974	32	36	33	33

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SUMMARY

Samples of bone ash are mixed with anhydrous copper sulphate and graphite and pelleted. A d.c. arc is used to excite the spectra which are then evaluated by microphotometry. The effective concentration range is 50 – 350 p.p.m. of strontium in the ash and the coefficient of variation is 6% for single exposures at the 90 p.p.m. level.

In the case of milk and vegetation, strontium and calcium are separated as insoluble oxalates and the strontium content of this fraction determined by a method similar to that used for bones, with a similar range and accuracy. An alternative flame photometric method is described for the determination of strontium in the calcium-strontium oxalate fraction, the coefficient of variation of the whole analytical operation being 5% per determination.

RÉSUMÉ

Une méthode spectrochimique est proposée pour le dosage du strontium dans les os, le lait et les plantes. La cendre d'os à analyser est mélangée à du sulfate de cuivre anhydre et à du graphite; ce mélange est ensuite comprimé et prêt pour la détermination spectrochimique. Dans le cas du lait et des plantes, le strontium doit être séparé préalablement sous forme d'oxalate.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur spektralanalytischen Bestimmung von Strontium in Knochen, Milch und Pflanzen. Bei der Untersuchung von Knochen wird deren Asche mit wasserfreiem Kupfersulfat und Graphit zu Pillen gepresst. Bei Milch und Pflanzen muss das Strontium vor der Bestimmung als Oxalat abgetrennt werden.

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CATION-EXCHANGE BEHAVIOUR OF URANIUM(VI) ON AMBERLITE IR-120

SEPARATION FROM MIXTURES

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Uranium(VI) forms strong anionic complexes of the type $[UO_2(CO_3)_3]^{-4}$ in carbonate solutions and $[UO_2(SO_4)_n]^{2-2n}$ where $n = 2$ or 3 in sulphuric acid solutions. The anion exchangers, Amberlite IRA-400[1] and Dowex A-1[2] have been used to recover uranium from the carbonate and sulphate leach systems. On the same principle uranium has been separated from bismuth[3]. Uranium(VI) also forms anionic chloro- and nitrato-complexes and has thus been separated on anion exchangers from vanadium[4], iron[5] etc. DOLAR AND DRAGANIC[6] have reported the separation of traces of rare earths from uranium(VI) on the cation-exchange resin, Amberlite IR-120. Uranyl ion is eluted by 0.5 *M* oxalic acid, and the rare earths by 5 *N* hydrochloric acid.

In this paper systematic quantitative studies on the behaviour of uranium(VI) on the cation exchanger, Amberlite IR-120, are described, with hydrochloric, nitric, sulphuric, acetic, citric and perchloric acids as eluting agents. Uranium has been separated from thorium, zirconium, cerium(III), mercury, copper, nickel and phosphate.

APPARATUS AND REAGENTS

Apparatus

Hilger Quartz spectrophotometer and 1-cm cells and a Cambridge pH indicator.

Ion-exchange column: The column used was of a U-shape and consisted of a glass tube (14 mm × 30 cm), flared at the top into a bulb (24 mm diameter) and extending from the bottom into the other limb (4 mm × 27 cm). The latter had a horizontal extension (5 cm), bending vertically downwards, and fitted with a stopcock to regulate the flow of liquid down the column. A resin bed, 1.4 × 14.5 cm, was employed.

Reagents

Uranyl nitrate stock solution, approximately 1 mg per ml; 2.1 g of uranyl nitrate hexahydrate (Mallinckrodt, A.R.) were dissolved in 1 l of water containing about 1% nitric acid. The solution was standardized by the oxine precipitation method. The stock solution contained 0.85 mg of uranium per ml. A solution containing 0.17 mg of uranium per ml was prepared by dilution and used for the ion-exchange runs. 8-Quinolinol (B.D.H., A.R.): 1% solution in chloroform. Buffer solution (pH 6.0): 77 g of ammonium acetate (E. Merck, Analar) were dissolved in water and glacial acetic acid and ammonia were added to adjust the pH to 6.0 with the aid of a Cambridge pH meter. The solution was diluted to 1 l and the pH was checked. Amberlite IR-120 (Rohm and Haas Company, Philadelphia), 20 to 50 mesh, hydrogen-form cation-exchange resin. The resin was conditioned by repeated washes with 4 *N* hydrochloric acid, followed by water. After being filled, the column was washed at a flow rate of 2 ml/min with 4 *N* hydrochloric acid, and then with water till the effluent became chloride-free. At the conclusion of the runs, the resin was withdrawn from the column, air-dried, dried in an oven at 100° for 1–2 h and weighed.

Chemicals used were all of reagent grade, unless otherwise mentioned.

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EXPERIMENTAL, RESULTS AND DISCUSSION

Ion-exchange behaviour studies

An aliquot of the uranyl nitrate solution containing 1.7 mg of uranium was passed through the resin bed at a rate of 2 ml per min. The resin was washed with 50 ml of water, and the uranium eluted with 200 ml of the different eluants. The latter included hydrochloric acid (1, 2, 3, 4 *N*), nitric acid (1, 2, 4 *M*), sulphuric acid (1, 2 *M*), acetic acid (2 *N*), perchloric acid (2 *M*) and citric acid (2%, 5%). In each case the elution rate was 2 ml per minute and the eluate was collected in 50-ml fractions. Each fraction was evaporated to dryness in a beaker, 10 ml of nitric acid, 5 ml of sulphuric acid and 1 to 2 ml of perchloric acid (60%) were added and the mixture evaporated again to dryness to destroy any organic matter from the resin. The residue was taken up with 5 ml of 1 *N* acetic acid, warmed and transferred to a separatory funnel. The sides of the beaker were rinsed with 10 ml of buffer solution of pH 6.0 and the washings transferred to the separatory funnel. The uranium was extracted with 8-quinolinol–chloroform and measured spectrophotometrically at 430 mμ[7]. The elution constant, E, for each eluting agent is calculated from the relation[8]:

$$E = \frac{d \cdot A}{V}$$

where V is the volume of eluant (corrected for non-effective liquid in the resin bed) which is required to displace uranium under essentially equilibrium conditions through a distance, d cm, in a column of known cross-sectional area, A cm².

TABLE I

BEHAVIOUR OF URANIUM(VI) TOWARDS VARIOUS ELUTING AGENTS

Weight of oven-dried resin = 7.2710 g

No.	*Eluting agents*	*Uranium recovery, %, (50-ml fractions of effluent)*				*Total uranium recovery %*	*Elution constant*
		I	*II*	*III*	*IV*		
1	HCl, 1 *N*	1.2	29.4	38.2	29.4	98.2	0.1628
	HCl, 2 *N*	0.3	44.0	50.0	6.0	100.3	0.1628
	HCl, 3 *N*	58.8	29.4	11.0	1.2	100.2	0.6009
	HCl, 4 *N*	64.2	24.5	8.9	2.9	98.0	0.6009
2	HNO_3, 1 *M*	0.8	28.6	32.4	35.3	97.1	0.1192
	HNO_3, 2 *M*	38.2	47.1	8.9	5.9	100.1	0.2561
	HNO_3, 4 *M*	44.1	44.2	11.8	2.0	99.1	0.6009
3	H_2SO_4, 1 *M*	70.6	23.5	5.0	0.0	99.1	0.6009
	H_2SO_4, 2 *M*	76.8	22.0	1.0	0.0	99.8	0.6009
4	$HClO_4$, 2 *M*	—	—	—	—	63.0	—
5	CH_3COOH, 2 *N*	—	—	—	—	58.9	—
6	Citric acid, 2%	—	—	—	—	58.8	—
	Citric acid, 5%	—	—	—	—	24.7	—

The results are shown in Table I. The elution curves obtained with hydrochloric, nitric and sulphuric acids are illustrated as histograms in Fig. 1.

With 200 ml of hydrochloric acid (2–4 *N*), nitric acid (2–4 *M*) or sulphuric acid (1–2 *M*) as the eluting agent, essentially quantitative recovery of uranium was possible. It is quite evident that an increase in the eluant volume from 200 ml to 300 ml will lead to 100% recovery of uranium (Nos. 1–3). In Fig. 1 the elution peak is gradually shifted towards the left with increased acid concentration. In Nos. 4–6 (Table I) the uranium recovery was incomplete with 200 ml of the eluting agents, and the elution peaks were not ascertained; probably they could be traced beyond an eluate volume of 200 ml. The elution constants (Table I) give a measure of the relative efficiency of the various eluants. The higher the value of the elution constant, the more efficient is the elution *i.e.*, the smaller is the volume of the eluting agent required. The eluting agents can be arranged in order of decreasing efficiency: sulphuric acid > hydrochloric acid > nitric acid > perchloric acid > acetic acid. This can be correlated with the strength of the complex formed between uranium and the eluting agent. The formation constants for UO_2SO_4, UO_2Cl^+ and $UO_2NO_3^+$ are 76, 0.88 and 0.24 respectively[9]. However, for routine work hydrochloric acid (2–4 *N*) is preferred owing to its ease of volatility in the assaying step. The whole operation takes 3 to 4 h. Organic acid eluants like citric or oxalic acid would involve time-consuming procedures.

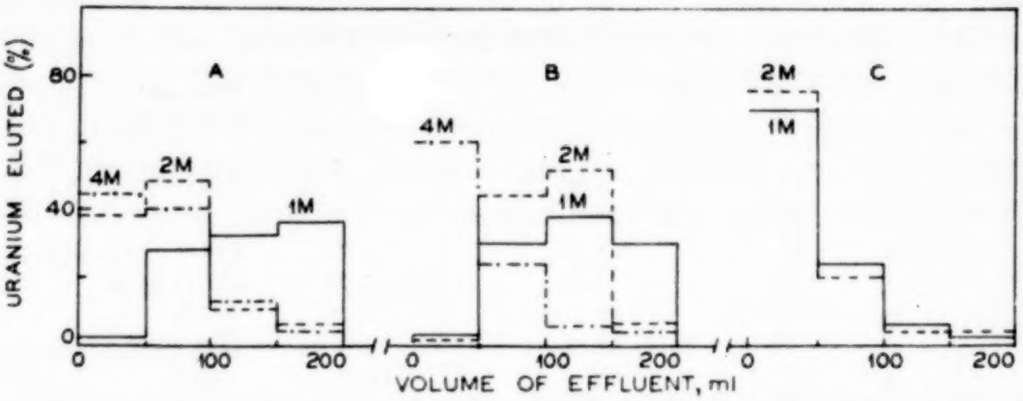

Fig. 1. Elution of uranium(VI) from Amberlite IR-120 resin. A. HNO_3, B. HCl, C. H_2SO_4.

Ion-exchange separations

Uranium is separated from various mixtures under conditions such that uranium remains as a cation and the added ion (or ions) is converted to a stable anionic complex. With such mixtures, uranium is retained on the resin bed, whereas the added ion passes through. Uranium can also be isolated from metals like thorium by selective elution with a mineral acid after adsorption on a cation-exchanger.

Separation from thorium

Thorium is more strongly adsorbed than uranium on a cation-exchanger and must be eluted with stronger acids. A mixture of uranyl and thorium nitrates in varying proportions was passed down the resin column. After washing with water (50 ml), uranium was eluted with 300 ml of 1 *N* hydrochloric acid and then thorium with 300 ml of 3 *M* sulphuric acid. The separate eluates containing uranium and thorium were diluted to 500 ml and suitable aliquots taken for analysis. Uranium was estimated spectrophotometrically as before and thorium by the Alizarin S method[10]. Quantitative recoveries of uranium were obtained on samples with uranium to thorium ratios from 1:0.9 to 1:8.8 (Table II).

TABLE II

ION-EXCHANGE SEPARATIONS

No.	*Taken mg*		*Found mg*		*Uranium recovery %*
1	U	1.7	U	1.7	100
	Th	1.5	—		
2	U	1.7	U	1.72	101.2
	Th	7.5	Th	7.75	(Th 103.3)
3	U	1.7	U	1.75	102.9
	Th	15.0	Th	15.0	(Th 100)
4	U	17	U	16.6	97.7
	Th	1.5	—		
5	U	24.5	U	24.94	101.8
	Zr	25			
6	U	24.5	U	25.0	102.1
	Zr	100			
7	U	24.5	U	24.0	97.95
	Ce(III)	25.0			
8	U	1.7[a]	U	1.75	102.9
	Hg	13.0			
9	U	24.5	U	25.1	102.4
	Hg	50			
10	U	24.5	U	25.9	105.7
	Cu	51.0			
	Ni	51.0			
11	U	24.5	U	25.72	104.9
	Phosphate	100			
12	U	24.5	U	24.74	100.9
	Phosphate	250			

[a] Uranium estimated by colorimetric method.

The separation factors for uranium/thorium (Table III) are obtained from their elution constant ratios. Only the values with hydrochloric and sulphuric acids as eluting agents are given. With 1 *N* hydrochloric acid the separation factor is very large; thorium is not eluted and quantitative separation is feasible. This was confirmed by the experimental results. The elution constants for thorium were determined as in case of uranium except that thorium was estimated colorimetrically with Alizarin S[10].

TABLE III

SEPARATION FACTORS FOR URANIUM/THORIUM

No.	*Eluting agent*	*Elution constant (E)*		*Separation factor* $\alpha = E_U/E_{Th}$
		Uranium	*Thorium*	
1	HCl, 1 *N*	0.163	∼ 0.0	∞
2	HCl, 6 *N*	0.601	0.256	2.35
3	H_2SO_4, 1 *M*	0.601	0.256	2.35
4	H_2SO_4, 3 *M*	0.601	0.601	1.00

Separations from zirconium, mercury, cerium(III), copper and nickel

Zirconium (as zirconyl oxychloride) was converted to an anionic complex with oxalic acid, mercury (mercuric chloride) with potassium iodide, and cerium(III) (as cerous chloride: cerous oxalate dissolved in hot dilute hydrochloric acid and filtered), copper (as the sulphate) and nickel (as the sulphate), with EDTA. After this pre-treatment the mixture was poured down the Amberlite IR-120 column (1.4 cm × 19.5 cm). The anionic complex passed out, the resin was washed with water till free from the excess of complexing agent, and uranium was eluted with 250 ml of 4 *N* hydrochloric acid. In each case the effluent was evaporated nearly to dryness with nitric and perchloric acids, and uranium estimated gravimetrically by the oxine method[11].

Separation from phosphate

When a mixture of uranyl nitrate and disodium hydrogen phosphate was passed through the cation exchanger, only uranium was adsorbed and could be eluted and estimated as above.

The separation of uranium from thorium is important in breeder reactors where the fissile material ^{233}U has to be separated from an intensely radioactive matrix of natural thorium. Zirconium and rare earths occur as major constituents of fission products and hence their isolation from irradiated reactor fuel (^{235}U) forms an important part of nuclear energy programmes. Phosphate is commonly associated with uranium in ores and as such its separation is significant. The proposed method can be adapted to large scale separations.

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SUMMARY

Quantitative studies are reported on the cation-exchange behaviour of uranium(VI) at the milligram level with Amberlite IR-120. Hydrochloric, nitric, sulphuric, perchloric, acetic and citric acids were tested as eluants; 200–300 ml of 2 *N* hydrochloric, nitric or sulphuric acid suffice for quantitative elution of 1.7 mg of uranium(VI) from a 1.4 cm × 14.5 cm bed. The efficiency of the eluting agents is discussed in terms of their elution constants. Uranium is separated from thorium by selective elution, from zirconium, cerium(III), copper and nickel by converting the latter into suitable anionic complexes and from phosphate just by passing the mixture through the cation exchanger.

RÉSUMÉ

Une étude quantitative a été effectuée sur le comportement de l'uranium(VI) sur une résine d'échange de cations. Il peut être alors séparé d'avec le thorium par élution sélective à l'aide d'un acide minéral; d'avec le zirconium, le cérium(III), le cuivre et le nickel en transformant ces derniers en complexes anioniques et d'avec le phosphate, simplement en faisant passer le mélange à travers l'échangeur de cations.

ZUSAMMENFASSUNG

Es wurde das Verhalten von Uran(VI) bei der Behandlung mit einem Kationenaustauscherharz quantitativ untersucht. Eine Trennung von Thorium kann durch selektive Eluierung mit einer Mineralsäure erzielt werden; zur Trennung von Zirkonium, Cer(III), Kupfer und Nickel werden diese in geeignete anionische Komplexe übergeführt; die Trennung von Phosphat erfolgt ohne weiteres beim Durchfliessen der Lösung durch die Kolonne des Kationenaustauschers.

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SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM WITH 9-METHYL-2,3,7-TRIHYDROXY-6-FLUORONE

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A sensitive method for the spectrophotometric determination of micro quantities of molybdenum(VI) is recommended which is based on the formation of a rose-red complex with 9-methyl-2,3,7-trihydroxy-6-fluorone.

Most of the colorimetric methods for molybdenum[1] are not sufficiently specific and preliminary separation is required. Acetyl acetone is a highly selective extractant for molybdenum, but a time-consuming wet oxidation[2] is required for its destruction before the determination of molybdenum. Extraction with α-benzoinoxime in chloroform and subsequent conversion to the quercetin complex[3] is long and tedious and vanadate and tungstate interfere seriously.

During study of phenolic derivatives as colour forming reagents[4,5], 9-methyl-2,3,7-trihydroxy-6-fluorone was found to be a very sensitive colorimetric reagent for molybdenum. The complex tends to precipitate from a slightly acid solution but this can be prevented by the presence of gelatin in 12% ethanol. The coloured compound is stable for at least 48 h and has its maximum intensity of colour at pH 1.5–2.3 with the maximum absorption at 510 mμ. The molar extinction coefficient of the complex is 24467. The system obeys Beer's law from 0.2 to 3 p.p.m. and the optimum range is from 0.8 to 3.0 p.p.m. of molybdenum, where the percent relative analysis error per

1% absolute photometric error, as calculated by Ayres method[6], is 2.8. The continuous variation and molar ratio methods indicate that the complex in solution contains the metal and the reagent in a ratio of 1:1, with an instability constant of about $2.09 \cdot 10^{-6}$ at 20°.

EXPERIMENTAL

Apparatus and solutions

The Uvispek spectrophotometer with 10.0-mm quartz transmission cells and the pH meter were as reported previously[5].

Reagent solution: Merck's reagent grade methyl fluorone (62.5 mg) was dissolved in a mixture of 210 ml of absolute alcohol and 12 ml of dilute sulphuric acid (1:6) and the solution made up to 250 ml with absolute alcohol.

Molybdenum solution: A standard molybdenum solution was prepared by dissolving a weighed amount of AnalaR ammonium molybdate in twice-distilled water and diluting to 500 ml. The molybdenum content of an aliquot portion of the solution was then determined gravimetrically with α-benzoinoxime. From this standard solution, more dilute solutions were prepared as required.

Buffer solution: A buffer of pH 2.0 was obtained by mixing solutions of *N* sodium acetate (50 ml) and *N* hydrochloric acid (52.5 ml) and diluting with water to 250 ml.

Equimolecular solutions of molybdenum and the reagent and a 0.4% (w/v) solution of gelatin were also prepared.

Solutions of various other ions were as used earlier[5].

Absorption spectra

An aliquot of standard solution containing 2 p.p.m. of molybdenum was transferred to a 25-ml volumetric flask; 1 ml of gelatin solution, 2 ml of reagent solution, 3 ml of absolute alcohol, and 3 ml of buffer solution were added. This order of addition was always maintained. A reagent blank without molybdenum was also prepared. The optical density of the test solution against both the reagent solution and distilled water and that of the blank against distilled water were measured at wavelengths from 470 to 600 mμ; the values are plotted in Fig. 1. The optical density had a maximum at 510 mμ, and all subsequent measurements were made at that wavelength.

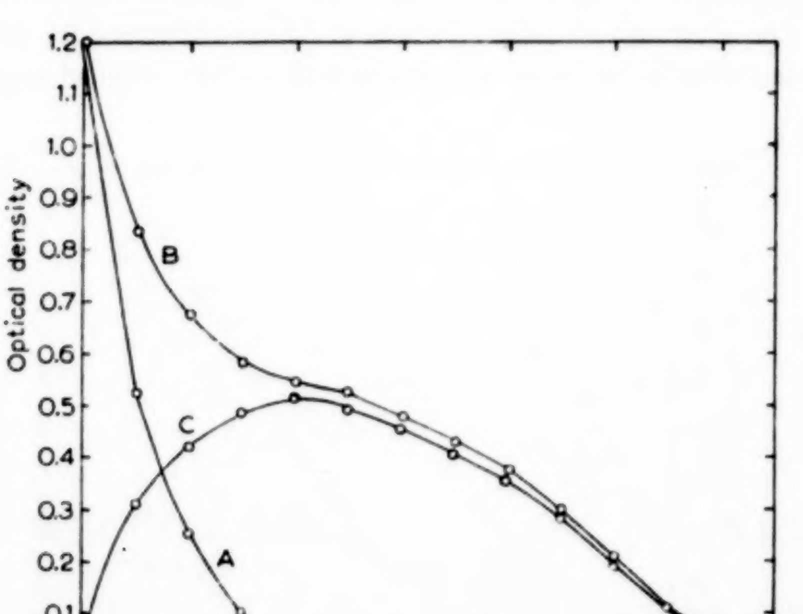

Fig. 1. Absorption spectra of reagent and its molybdenum complex. A. Reagent against water. B. Reagent plus molybdenum against water. C. Reagent plus molybdenum against reagent.

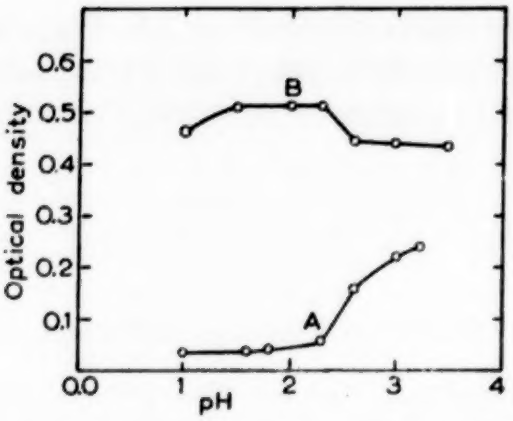

Fig. 2. A. Effect of pH on the reagent.
B. Effect of pH on the complex.

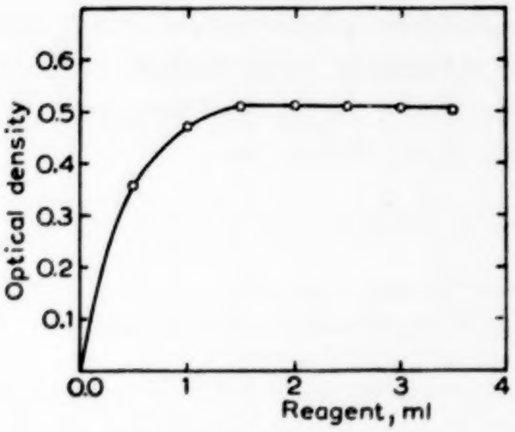

Fig. 3. Effect of reagent.

Variation of optical density with pH, reagent and time

The test and blank solutions were prepared at different pH values obtained by the addition of sulphuric acid or sodium acetate solution. The variation of the optical density of the test solutions (relative to the blank) and of the reagent solutions with pH is shown in Fig. 2 (curves A and B). The optical density is almost constant between pH 1.5 and 2.3; this range was used for all subsequent readings.

The effect of reagent concentration on optical density in presence of 2 p.p.m. of molybdenum is shown in Fig. 3. The maximum optical density is obtained only when the amount of the reagent solution is 1.5 ml or more; in all subsequent experiments, the volume of the reagent used was 2 ml. One ml of the gelatin solution was always added and the colour intensity was then found to be stable for 48 h at room temperature.

Beer's law, optimum range and photometric error

The optical density increases linearly with the concentration (0.2 to 3.0 p.p.m.) of molybdenum in accordance with Beer's law and the optimum concentration range, as obtained from the steepest slope of the curve (Fig. 4) drawn by plotting the percent absorptancy against the logarithm of concentration of molybdenum[7], is from 0.8 to

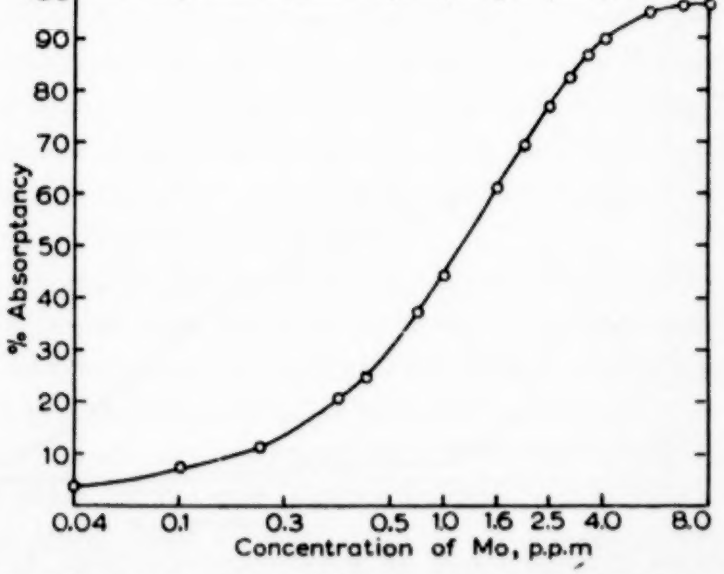

Fig. 4. Standard curve for molybdenum–methyl fluorone complex.

3 p.p.m. of molybdenum. The relative analysis error per 1% absolute photometric error for this range is 2.8%.

The ions listed in Table I do not affect the absorption of either the blank or the test solution. With ascorbic acid as a masking agent, ferric ion and vanadate can be tolerated up to 20 p.p.m. and 10 p.p.m. respectively.

Zirconium, titanium, chromate and tungstate interfere even when only 2 p.p.m. are present.

TABLE I

NON-INTERFERING IONS
Molybdenum concentration, 2 p.p.m.

Ion	*Maximum concentration investigated in p.p.m.*
Fluoride	10
Chloride	200
Nitrate	200
Perchlorate	200
Sulphate	400
Phosphate	10
Acetate	1000
Tartrate	200
Citrate	200
Oxalate	10
Ferrous (iron)	50
Uranyl	50
Aluminium	50
Sodium	500
Ammonium	200

Composition, molar extinction coefficient, degree of dissociation and instability constant

For the evaluation of composition of the complex, the absorption of mixtures of equimolecular solutions ($1 \cdot 10^{-4}$ M) of molybdenum and reagent were measured at 510 mμ. Fig. 5 shows the absorption (after proper corrections for the absorption of the reagent) plotted against increasing amounts of molybdenum. The sharp peak

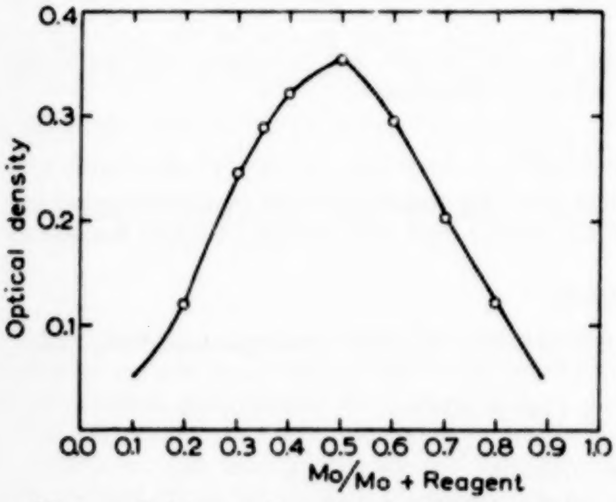

Fig. 5. Job's continuous variation curve.

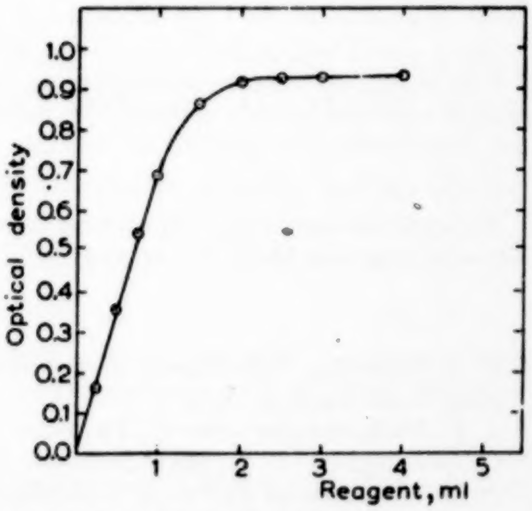

Fig. 6. Molar ratio method: $0.969 \cdot 10^{-3}$ M solutions of molybdenum and reagent.

in the curve indicates definite compound formation between the molybdenum and the reagent when present in a ratio of 1:1. The nature of the curve (Fig. 6) derived from the molar ratio method confirms the observation that the molybdenum and the reagent combine in a ratio of 1:1.

The molar extinction coefficient of the complex calculated from Beer's law curve is

$$\frac{0.510 \cdot 95.95 \cdot 10^3}{2} = 24467$$

The degree of dissociation, α, is calculated from the relationship[8]

$$\alpha = \frac{E_m - E_s}{E_m}$$

The E_m and E_s values are 0.510 and 0.372 respectively at a molybdenum concentration of $2.08 \cdot 10^{-5}$ M, and the degree of dissociation, α, is thus 0.2707. The instability constant, K, from the equation

$$K = \frac{\alpha^2 C}{1 - \alpha}$$

where C is the concentration of the complex in moles per l, is $2.091 \cdot 10^{-6}$.

ACKNOWLEDGEMENT

The authors wish to thank the University Grants Commission, Government of India, for providing the Hilger Uvispek spectrophotometer and the Cambridge pH meter.

SUMMARY

9-Methyl-2,3,7-trihydroxy-6-fluorone is proposed as a highly sensitive reagent for molybdenum. The rose-red complex shows maximum absorption at 510 mμ and obeys Beer's law from 0.2 to 3 p.p.m. of molybdenum, the optimum range being 0.8 to 3 p.p.m. where the percent relative analysis error is only 2.8. In solution the complex contains molybdenum and the reagent in the ratio 1:1. The instability constant of the complex is about $2.09 \cdot 10^{-6}$.

RÉSUMÉ

Une méthode spectrophotométrique pour le dosage du molybdène est proposée, utilisant un réactif nouveau et très sensible: la méthyl-9-trihydroxy-2,3,7-fluorone-6.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode zur Bestimmung von Molybdän beschrieben unter Verwendung von Methyl-9-trihydroxy-2,3,7-fluoron-6 als neues und sehr empfindliches Reagenz.

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THE USE OF LANTHANUM CHLORIDE TO PREVENT INTERFERENCES IN THE FLAME PHOTOMETRIC DETERMINATION OF EXCHANGEABLE CALCIUM IN SOILS

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INTRODUCTION

Flame photometry provides a simple and rapid means for the chemical analysis of calcium. However interferences from other ions present in the solution can occur which, unless suitable steps are taken to prevent them, may seriously affect the accuracy of the results. In the determination of calcium by flame excitation techniques, ions reported to cause such interferences include aluminium[1], phosphate[2-5], sulphate[5,6], and bicarbonate[6]. In addition the author has observed that silicate can cause serious interference. Sodium and potassium may also interfere, due to some transmission of their radiation if an interference filter is used to isolate the calcium radiation[7].

If soils are leached with normal ammonium chloride for the determination of exchangeable cations[8], all of these ions may be present in the leachate although generally only in very low concentration. In leachates from acid soils however, appreciable amounts of aluminium may be present, while in the leachates from calcareous soils bicarbonate may be present in quite high concentrations.

Such interferences may be overcome either by the removal of the interfering ions by precipitation or ion exchange, by adding an excess of the interfering ion, or by the addition of some other ion which may block the interference chemically. The latter two methods, being simpler, are generally preferred. The present investigation was undertaken to examine the possible extent of likely interferences on the determination of calcium in ammonium chloride leachates of soils, and to devise a suitable means of overcoming them.

EXPERIMENTAL

The results reported were obtained using an E.E.L. flame photometer with an interference filter to isolate the calcium oxide emission band at 620 mμ. The gases used were air and a proprietary bottled gas similar to "calor" gas.

Stock solutions were prepared as follows:

Calcium: calcium carbonate was dissolved in a slight excess of hydrochloric acid. The solution was boiled to expel carbon dioxide and, after cooling, made to volume with water.

Magnesium: magnesium metal powder was dissolved in a slight excess of hydrochloric acid and the solution adjusted to volume.

Aluminium: aluminium metal was dissolved in a slight excess of hydrochloric acid as for magnesium.

Phosphate, sulphate, bicarbonate and silicate solutions were prepared from potassium dihydrogen phosphate, ammonium sulphate, sodium bicarbonate and sodium silicate, respectively.

All other cations were prepared by solution of the chlorides.

Test solutions were prepared by mixing appropriate volumes of the stock solutions and adjusting to a final volume of 20 ml.

RESULTS

(a) *The effect of ammonium chloride concentration on calcium emission*

The results of varying concentrations of ammonium chloride on the intensity of the calcium emission are given in Table I.

TABLE I

THE EFFECT OF AMMONIUM CHLORIDE ON CALCIUM EMISSION

NH_4Cl normality	*Galvanometer reading*		
	12.5 p.p.m. Ca	*25 p.p.m. Ca*	*50 p.p.m. Ca*
0	17	33	66
0.2	15	31	62
0.4	15	30	60
0.6			59
0.8			57
1.0	14	28	55
2.0			48

These results show that ammonium chloride partially suppressed the calcium emission. Over the range of concentration 0.2 *N* to 2 *N* this suppression was directly proportional to the ammonium chloride concentration. Since in the majority of ammonium chloride leachates of soils the calcium concentration is likely to lie within a range suitable for analysis without dilution, all subsequent investigations were made in normal ammonium chloride.

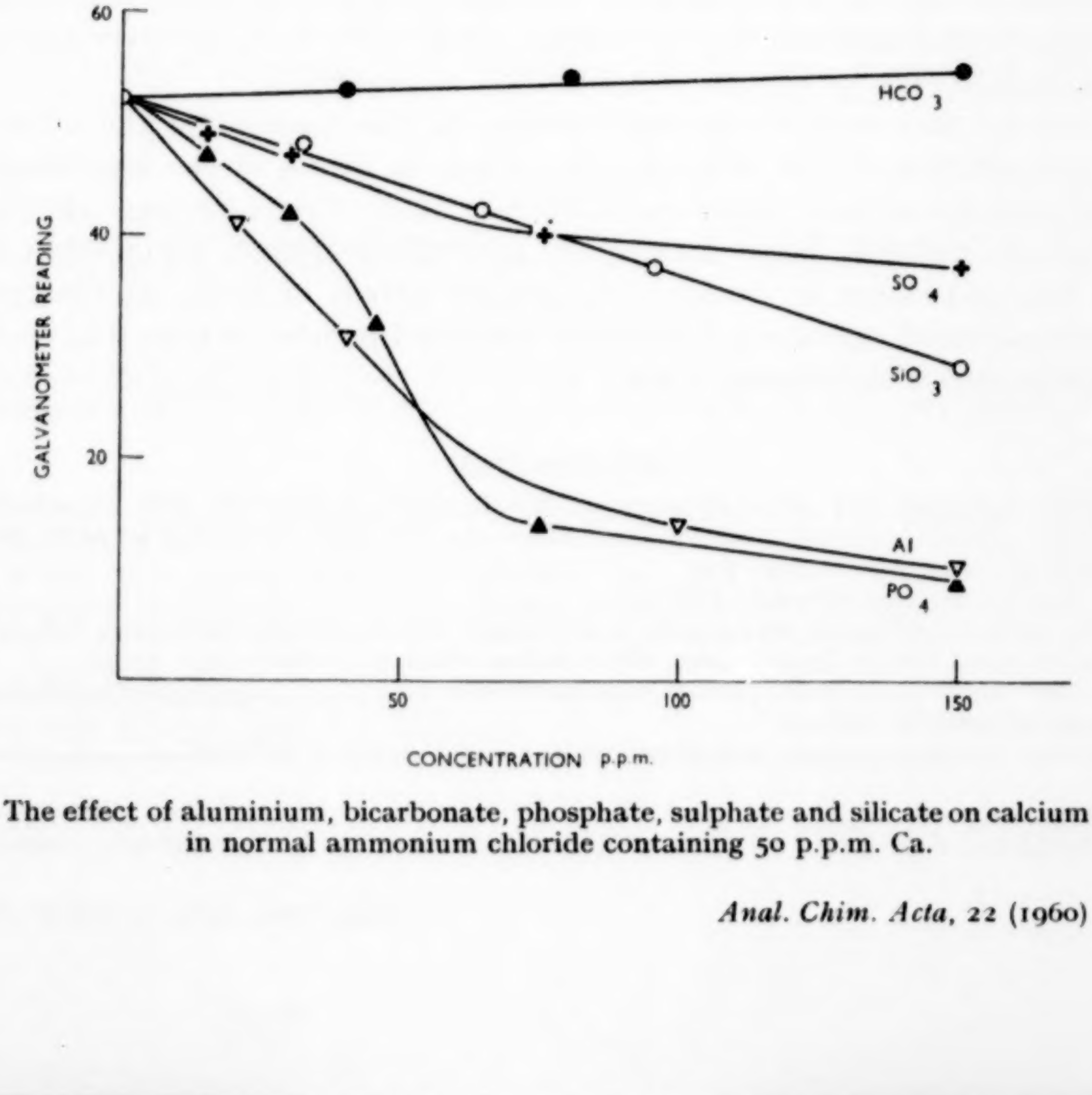

Fig. 1. The effect of aluminium, bicarbonate, phosphate, sulphate and silicate on calcium emission in normal ammonium chloride containing 50 p.p.m. Ca.

(*b*) *The effect of extraneous ions on calcium emission in normal ammonium chloride solutions*

Ions most likely to cause serious interference in the flame photometric determination of calcium include aluminium, bicarbonate, phosphate, sulphate and silicate. The results of an examination of the effect of varying concentrations of these ions on calcium emission in normal ammonium chloride solutions are shown in Fig. 1.

These results show that with the exception of bicarbonate, which showed a slight positive interference, each of the ions tested caused serious interference. With the majority of soils the concentration of each of these ions in the ammonium chloride leachate is likely to be low (generally less than 1–2 p.p.m.) so that their interference on the direct determination of calcium would be small. In very acid and alkaline soils however, greatly increased amounts of soluble aluminium are likely[9], and concentrations as high as 100 p.p.m. are possible in the ammonium chloride leachate. As is evident from Fig. 1 such concentrations of aluminium would make the direct determination of calcium on the leachate impossible.

(*c*) *Elimination of interferences*

Aluminium: As aluminium is likely to be the most serious interfering ion in ammonium chloride leachates initial investigations were directed towards overcoming interference from it.

MITCHELL AND ROBERTSON[1] found that the addition of strontium overcame the interference of aluminium with calcium in the Lundegardh technique for flame emission spectroscopy. DAVID[10] used magnesium to prevent similar interferences when using an atomic absorption flame spectrophotometric technique while YOFE AND FINKELSTEIN[5] have used lanthanum to overcome the interference of phosphate and sulphate on calcium. Tests were made to examine the possibility of using strontium, magnesium, lanthanum or barium to similarly overcome aluminium interferences under the present conditions of measurement. The results are given in Table II.

TABLE II

THE EFFECT OF BARIUM, STRONTIUM, LANTHANUM AND MAGNESIUM ON ALUMINIUM INTERFERENCE WITH CALCIUM IN NORMAL AMMONIUM CHLORIDE CONTAINING 50 p.p.m. CALCIUM

Cation added	*Galvanometer reading*				
	Aluminium added p.p.m.				
	0	*20*	*40*	*100*	*200*
Nil	52	41	31	14	9
Strontium[a] 1000 p.p.m.	85	83	80	71	64
Barium 1000 p.p.m.	62	50	42	30	26
Magnesium 1000 p.p.m.	42	44	46	20	17
Magnesium 2000 p.p.m.	44	44	44	43	21
Lanthanum 1000 p.p.m.	52	52	52	51	26
Lanthanum 2000 p.p.m.	52	52	52	52	49

[a] Sensitivity 1/3 of all other readings.

Sufficient strontium radiation, probably from the strontium oxide band at 680 mμ was transmitted by the radiation filter to cause serious interference with calcium and it was necessary to reduce the sensitivity to one third of that of the other readings in order to read these solutions. This fact alone is sufficient to exclude the use of strontium, but it is of interest to note also, that, under the present conditions of experiment, aluminium still interfered seriously with the radiation measured. Examination of calcium-free strontium solutions showed that much of the interference measured in the presence of strontium could have been due to the effect of aluminium on strontium emission. The failure of the radiation filter to exclude strontium radiation thus prevented observation of any effect of strontium on the aluminium interference with calcium emission.

Barium only slightly reduced the aluminium interference with calcium.

Both lanthanum and magnesium, however, showed a capacity to suppress aluminium interference. Since at the concentrations used magnesium slightly suppressed the calcium emission, and, as magnesium was less effective in suppressing the aluminium interference, lanthanum was chosen for further investigation. Further, magnesium is an exchangeable cation usually determined together with calcium and the choice of an element other than one of the test elements has obvious advantages.

In order to determine the optimum lanthanum concentration required to control aluminium interference, solutions of varying calcium, aluminium and lanthanum contents were examined. Aluminium concentrations ranged from 0 to 200 p.p.m. and lanthanum from 250 to 5000 p.p.m. The results, summarized in Fig. 2, showed that irrespective of calcium, aluminium or lanthanum concentration, aluminium interference was eliminated provided the ratio of lanthanum to aluminium was equal to or greater than 12.5:1. This corresponds to an atomic ratio of approximately 2.5:1.

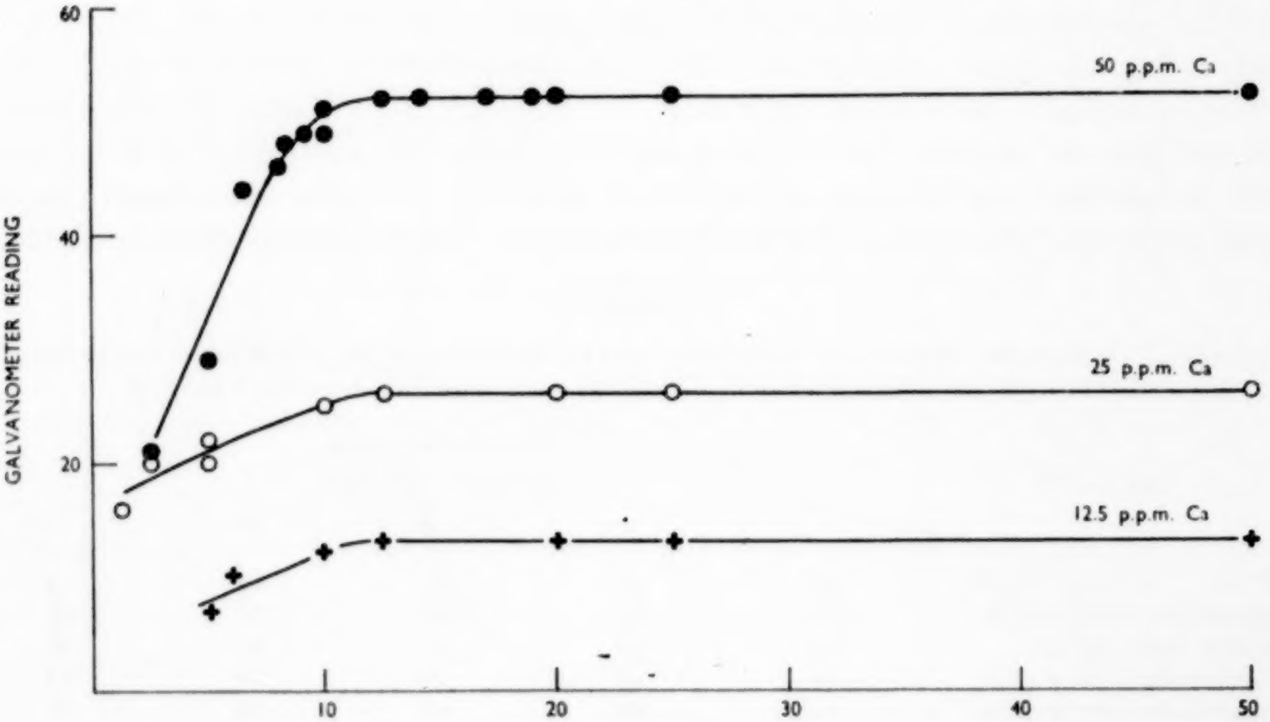

Fig. 2. The effect of lanthanum on aluminium interference with calcium emission in normal ammonium chloride.

On the basis of these results 2000 p.p.m. of lanthanum was chosen as a working concentration adequate to prevent all likely interference from aluminium in natural soil leachates. The effectiveness of 2000 p.p.m. of lanthanum in overcoming aluminium interference is shown in Table III.

TABLE III

THE EFFECT OF 2000 p.p.m. OF LANTHANUM ON ALUMINIUM INTERFERENCE WITH CALCIUM IN NORMAL AMMONIUM CHLORIDE SOLUTION

Aluminium p.p.m.	*Galvanometer readings*						*Aqueous solution 50 p.p.m. Ca*
	12.5 p.p.m. Ca		*25 p.p.m. Ca*		*50 p.p.m. Ca*		
	−La	*+La*	*−La*	*+La*	*−La*	*+La*	
0	13	13	26	26	52	52	66
20	5	13	16	26	41	52	46
40	2	13	10	26	31	52	32
100	2	13	4	26	14	52	14
160				26		52	
200	2	12	4	25	10	49	9

At each level of calcium 2000 p.p.m. of lanthanum completely prevented interference up to 160 p.p.m. of aluminium.

Bicarbonate: Calcium carbonate is slightly soluble in ammonium chloride so that bicarbonate concentrations of the order of 200–300 p.p.m. could be encountered in the leachates of calcareous soils. Table IV gives results showing the effect of varying concentrations of bicarbonate on calcium emission.

TABLE IV

THE EFFECT OF 2000 p.p.m. OF LANTHANUM ON BICARBONATE INTERFERENCE WITH CALCIUM IN NORMAL AMMONIUM CHLORIDE SOLUTION

Bicarbonate p.p.m.	*Galvanometer readings*				*Aqueous solution 50 p.p.m. Ca*
	25 p.p.m. Ca		*50 p.p.m. Ca*		
	−La	*+La*	*−La*	*+La*	
0	26	26	53	53	66
40	26	26	53	53	54
80	26	26	54	55	44
160	28	27	55	55	39
200	27	27	56	55	29
400	29	29	57	58	

These results show that whereas bicarbonate interfered quite seriously with calcium in aqueous solutions, the only effect in normal ammonium chloride solution both in the presence and absence of lanthanum was a small positive interference. This was found to be largely due to traces of calcium impurity in the bicarbonate reagent together with slight interference from sodium.

Phosphate, sulphate and silicate: Table V gives results showing the effects of phosphate, sulphate and silicate on calcium emission in the presence and absence of 2000 p.p.m. of lanthanum.

The addition of 2000 p.p.m. of lanthanum completely suppressed phosphate interference at all levels tested up to 150 p.p.m. While lanthanum greatly reduced the interference from sulphate it did not completely suppress it. Sulphate interference in the presence of lanthanum however was small and at the low concentrations likely to be present in soil leachates it would be negligible.

In aqueous solution silicate interfered seriously with calcium emission. In normal ammonium chloride solution this interference while still serious was considerably

TABLE V

THE EFFECT OF 2000 p.p.m. OF LANTHANUM ON THE INTERFERENCES OF PHOSPHATE, SULPHATE AND SILICATE WITH 50 p.p.m. OF CALCIUM IN NORMAL AMMONIUM CHLORIDE SOLUTION

Concentration of interfering ion p.p.m.	*Galvanometer reading*								
	Phosphate			*Sulphate*			*Silicate*		
	Aqueous solution	*N NH_4Cl*	*N NH_4Cl + La*	*Aqueous solution*	*N NH_4Cl*	*N NH_4Cl + La*	*Aqueous solution*	*N NH_4Cl*	*N NH_4Cl + La*
0	66	53	53	66	52	52	66	52	52
15	58	47	53	58	49	51	45	50	52
30	50	42	52	53	47	48	33	48	52
75	15	14	52	42	40	49	7	40	52
150	11	9	52	39	37	48	3	28	52
300	9	8	43				2	5	44

reduced. The addition of 2000 p.p.m. of lanthanum however completely suppressed interference from silicate at all levels tested up to 150 p.p.m. SiO_3.

Examination of solutions containing mixtures of aluminium, phosphate, sulphate, and silicate showed that in the presence of 30 p.p.m. of phosphate, 30 p.p.m. of sulphate and 12.5 p.p.m. of silicate (concentrations greatly in excess of those likely in soil leachates) aluminium concentrations could be increased to 100 p.p.m. without causing interference if 2000 p.p.m. of lanthanum were present. Thus it is apparent that the addition of 2000 p.p.m. of lanthanum to ammonium chloride leachates of soils would prevent all likely interference from these ions.

Other ions: Other ions likely to be present in ammonium chloride leachates of soils include sodium, potassium, magnesium, and, in the case of acid soils, iron and manganese. Examination of the effects of various concentrations of these ions on calcium emission in normal ammonium chloride containing 2000 p.p.m. of lanthanum showed that both sodium and potassium caused slight positive interferences with calcium. Enhancement of calcium emission was found equivalent to approximately 1 p.p.m. of calcium for each 100 p.p.m. of sodium, while the interference from potassium was found to be approximately half that of sodium. At the concentrations normally to be expected in soil leachates these interferences would be small, and, if average amounts were included as a background in the standard solutions used for preparation of the calibration lines, interference from these ions would be reduced to negligible proportions. Magnesium, which at higher concentrations in the absence of lanthanum (Table II) caused a small suppression of calcium emission, caused no interference in concentrations up to 200 p.p.m., while iron and manganese at concentrations of 100 p.p.m. also caused no interference.

(*d*) *The effect of lanthanum on the determination of sodium, potassium and magnesium*

Sodium, potassium and magnesium are usually determined in the ammonium chloride leachate in addition to calcium.

An examination of a range of normal ammonium chloride solutions containing these elements was made both in the presence and absence of 2000 p.p.m. of lanthanum. Sodium and potassium were determined using the E.E.L. flame photometer and magnesium by atomic absorption flame spectrophotometry in a manner similar to that described by DAVID[10].

This showed that addition of lanthanum had no effect on the sodium and magnesium readings but increased the potassium readings slightly. This increase, corresponding to 0.4 p.p.m. of potassium, was probably due to potassium impurity in the lanthanum chloride. Thus it is clear that the addition of lanthanum would have no detrimental effects on the determination of sodium, potassium or magnesium using the methods described.

(e) *The effect of fungicides*

If leachates are to be retained for more than one or two days before analyses are made it is generally desirable to add a preservative to prevent mould growth. An examination of a number of fungicides was therefore made for their effect on the determination of calcium, sodium and potassium.

Alcohol (1 ml per 100 ml of N NH_4Cl) caused an enhancement in each case while chloroform (0.1 ml per 100 ml) caused a depression. Toluene (0.1 ml per 100 ml), 36% formaldehyde (0.2 ml) and mercuric chloride (1.0 g) did not affect any of the readings.

RECOMMENDED PROCEDURE

On the basis of the preceding results, the following procedure for determination of exchangeable calcium in soils was adopted.

Leach 10 g of soil with normal ammonium chloride by the procedure described by PIPER[8], collecting the leachate in a 200-ml volumetric flask until approximately 190 ml of leachate has been collected. Add 0.4 ml of 36% formaldehyde solution and 5 ml of a 21.3% solution of a lanthanum chloride ($LaCl_3 \cdot 7H_2O$) and adjust to volume. In view of possible interference resulting from alcohol it is essential that all alcohol be removed before addition of ammonium chloride after the alcohol washing to remove soluble salts.

Prepare suitable calcium standards ranging from 0 to 100 p.p.m. of calcium in normal ammonium chloride containing 2000 p.p.m. of lanthanum, 5 p.p.m. of sodium, 10 p.p.m. of potassium and 25 p.p.m. of magnesium. Leachates can then be read on the flame photometer and calcium concentrations determined from the calibration curve. If, in the case of soils high in exchangeable calcium, a dilution is necessary, this should either be made using normal ammonium chloride containing 2000 p.p.m. of lanthanum, or if the dilution is made with water, a fresh set of standards must be prepared to correspond with the diluted samples.

Comparison with other methods

To check the reliability of the proposed method a group of soils was leached with normal ammonium chloride, but, to enable comparisons to be made, no lanthanum chloride was added before adjusting to volume. 20-ml aliquots of the leachates were taken and 1 ml of lanthanum or magnesium chloride solutions added to give final concentrations of 2000, 1000 and 500 p.p.m. of lanthanum and 2000 p.p.m. of magnesium. These were measured with the flame photometer in the usual way and calcium estimated by reading from corresponding calibration lines. In addition, calcium was estimated by direct reading of the ammonium chloride leachate without treatment.

A further series of 20-ml aliquots was taken in 50-ml centrifuge tubes, 2 drops of a ferric chloride solution containing 100 mg of iron per ml were added to each and then 5 ml of $N/8$ ammonium hydroxide. After shaking to mix they were allowed to stand overnight and then centrifuged. The supernatant liquors were then read on the flame photometer and calcium estimated from a corresponding calibration curve.

Exchangeable calcium was also determined on a separate leachate by the oxalate-titration method of PIPER[8]. Aluminium in the leachates was determined by the method of JONES AND THURMAN[11]. These results are given in Table VI.

TABLE VI

EXCHANGEABLE CALCIUM IN SOILS AS DETERMINED BY DIFFERENT PROCEDURES

Soil No.	1	2	3	4	5	6	7
Soil pH	5.21	5.28	5.08	5.00	4.06	5.02	4.18
Aluminium in leachate p.p.m. Al	0.4	2.3	7.0	7.1	28.5	31.5	45.0
Procedure	*Calcium m.e. per 100 g*						
Oxalate-titration	3.96	4.82	0.60	1.47	1.48	1.08	1.22
Direct[a]	3.65	4.30	0.34	0.69	0.50	0.18	0.18
+ 2000 p.p.m. La	3.95	4.70	0.50	1.24	1.40	1.00	1.40
$Fe(OH)_3$ precipitation	4.19	4.56	0.50	1.20	1.42	1.00	1.20
+ 1000 p.p.m. La	3.90	4.65	0.50	1.20	1.50	1.00	1.17
+ 500 p.p.m. La	3.95	4.40	0.50	1.24	1.40	1.00	1.09
+ 2000 p.p.m. Mg	4.00	4.51	0.50	1.24	1.24	0.89	0.89

[a] Flame photometric determination directly on the ammonium chloride leachate.

These results show that the direct estimation of calcium in ammonium chloride without steps to prevent interferences can lead to highly erroneous results. The addition of lanthanum to the solution, however, yielded results which agreed satisfactorily with those obtained by the oxalate-titration method and by the method in which aluminium was co-precipitated with ferric hydroxide indicating that the lanthanum had fully prevented all interferences with calcium emission. Magnesium was less effective, particularly in the soils high in soluble aluminium.

DISCUSSION

The results show that aluminium, phosphate, sulphate and silicate can each cause serious interferences in the flame photometric determination of calcium in ammonium chloride solutions. All can be prevented by the addition of lanthanum to the solution. The mechanism of these interferences is by no means fully understood but probably a major factor in them is the formation of compounds which are stable at high temperature and which prevent the test element from reaching an excited state in the flame. LEYTON[3] showed that the formation of tricalcium phosphate in the flame was a likely reason for the interference of phosphate with calcium emission. Similar reasons can be advanced to explain a major part of the interferences resulting from aluminium, sulphate and silicate.

YOFE AND FINKELSTEIN[5] suggested that the mechanism by which lanthanum prevented the interference of phosphate and sulphate with calcium was by the formation of lanthanum phosphate and sulphate both of which had greater thermostability than the corresponding calcium compounds. Since the present results show that, irrespective of calcium, lanthanum or aluminium concentration, a minimum atomic ratio of lanthanum to aluminium of 2.5:1 is necessary to suppress aluminium interference, it seems likely that a similar mechanism operates in preventing aluminium interference.

In ammonium chloride leachates of soils the phosphate, sulphate and silicate concentrations would not often reach a level at which serious interference with calcium would result. However, in leachates from acid soils and possibly also from highly alkaline soils aluminium concentrations can reach levels which would cause serious interference. The results show that 2000 p.p.m. of lanthanum would prevent all likely interference from aluminium, phosphate, sulphate and silicate in soil leachates. For soils other than those of very low or high pH the amount of lanthanum could probably be reduced to half, or even less, of this amount.

As lanthanum chloride had no adverse effect on flame photometric determinations of sodium, potassium and magnesium it could, if desired, be added directly to the ammonium chloride leachate before adjusting to volume.

The slight interference from sodium and potassium would be negligible at concentrations normally to be expected in soil leachates and the incorporation of average concentrations in the background solutions for the standards would reduce interference to negligible proportions.

Results obtained on a group of soils show that values obtained by the proposed method agreed satisfactorily with values obtained by an oxalate-titration method.

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SUMMARY

An examination of the interferences of aluminium, bicarbonate, phosphate, sulphate and silicate in the flame photometric determination of calcium in ammonium chloride solutions has shown that, with the exception of bicarbonate, all cause serious interference. Addition of lanthanum to the solution can satisfactorily prevent each of these interferences. Provided the lanthanum to aluminium ratio is at least 12.5:1 by weight all interference from aluminium can be prevented. The use of lanthanum chloride to prevent such interferences in the determination of calcium in ammonium chloride leachates of soils is discussed and a simple flame photometric method for the determination of exchangeable calcium in soils is proposed.

RÉSUMÉ

Une méthode simple, par photométrie de flamme, est décrite pour le dosage du calcium dans les terres. L'emploi du chlorure de lanthane permet de rendre ce dosage plus sélectif.

ZUSAMMENFASSUNG

Es wird gezeigt, dass bei der flammenphotometrischen Bestimmung von Calcium in Bodenproben starke Störungen verursacht werden durch gleichzeitig vorhandenes Aluminium, Phosphat, Sulfat und Silikat. Durch Zusatz von Lanthanchlorid lassen sich die Störungen weitgehend ausschalten.

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STUDIES OF THE SOLVENT EXTRACTION OF CADMIUM AND SILVER DITHIZONATES

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INTRODUCTION

History of dithizonate extractions

Although dithizone is a very good reagent for the analytical determination of a large number of metal ions and although metal dithizonates have been studied in an empirical manner quite extensively, only in relatively recent times systematic studies of the equilibria associated with the solvent extraction of metal dithizonates have been made. Wichman[1] first called attention to the importance of extraction or equilibrium curves (per cent metal extracted *versus* pH) for analytical purposes. Kolthoff and Sandell[2] studied the extraction of zinc dithizonate and derived some equations to describe the extractions of divalent metal ions. Irving and Williams[3] and Furman, Mason and Pekola[4] later derived some expressions which were more general and which applied to systems in which extraction proceeds as it does in the case of dithizonate extractions. Even though the equilibria involved in the solvent extraction of metal dithizonates now appear to be well understood, the amount of quantitative data for the various metal dithizonate systems remains small. Systematic studies providing pertinent constants have been made with zinc dithizonate[2,5,6], copper dithizonate[7,8], silver dithizonate[8,9], and mercury dithizonate[10].

History of extraction equations

The equation

$$E = \frac{P_r^n K_r^n (\mathrm{HR})_o^n}{P_c P_r^n K_r^n (\mathrm{HR})_o^n + P_c K_c (\mathrm{H})^n} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

was derived by Irving and Williams[3] in 1949 to describe the solvent extraction process for two phase systems initially made up of an aqueous phase containing a metal ion and hydrogen ion and a non-aqueous phase containing a complexing agent. In equation (1) E designates the ratio of metal concentration in the non-aqueous phase to the metal concentration in the aqueous phase and is referred to as the extractability; P_r and P_c designate the partition coefficients of the complexing agent and the metal complex respectively; K_r designates the ionization constant of the complexing agent; K_c designates the dissociation constant of the metal complex; $(\mathrm{HR})_o$ designates the concentration of the complexing agent in the organic phase; (H)

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designates the concentration of the hydrogen ion in the aqueous phase; and n designates the valence of the metal ion. In this paper the subscript o will be used to show that a specie is in the non-aqueous phase; other species are in the aqueous phase. In cases in which P_c is very small equation (1) may be written as

$$E = \frac{P_r^n K_r^n (\mathrm{HR})_o^n}{P_c K_c (\mathrm{H})^n} = \frac{K(\mathrm{HR})_o^n}{(\mathrm{H})^n} \quad \text{(2)}$$

where the constant K is given by

$$K = \frac{P_r^n K_r^n}{P_c K_c} \quad \text{(3)}$$

K is thus the equilibrium constant for the extraction reaction which may be written as

$$\mathrm{M} + n\mathrm{HR}_{(o)} = \mathrm{MR}_{n(o)} + n\mathrm{H} \quad \text{(4)}$$

In equation (4) the terms M and H are the metal ion and the hydrogen ion respectively in the aqueous phase, and HR and MR_n are the complexing agent and the metal complex respectively in the non-aqueous phase. The charges of ions have been omitted so that the writing of equations might be simplified. KOLTHOFF AND SANDELL[2] in 1941 derived an equation which is equivalent to equation (2). SCHWEITZER AND HONAKER[6] made use of this equation in their study of zinc dithizonate extractions.

By taking the logarithm of equation (2) IRVING AND WILLIAMS obtained the following relation at 50% extraction

$$\mathrm{pH}_{\frac{1}{2}} = -\log K - n \log (\mathrm{HR})_o \quad \text{(5)}$$

where $\mathrm{pH}_{\frac{1}{2}}$ designates the pH at which 50% extraction is obtained.

History of masking studies

The effect on extractions of species in the aqueous phase which react with the metal ion to form water soluble complexes has been studied systematically very little. Such extractions are usually referred to as masked extractions, and a substance in the aqueous phase which forms water soluble complexes with the metal ion or ionizes to form ions which in turn form water soluble complexes with the metal ion is called a masking agent. In this work the water soluble complexes will be referred to as masking complexes.

CONNICK AND MCVEY[11] in 1949 studied the masking effect of various anions on the extraction of zirconium(IV) with thenoyltrifluoroacetone and were able to obtain the stability constants of the masking complexes. RYDBERG[12] in 1950 made a study of the complexes which are formed between thorium(IV) and acetylacetone by extracting thorium tetraacetylacetonate into benzene. RYDBERG gave a very excellent treatment of some methods for finding stability constants of masking complexes. In RYDBERG's experiments the complexes which correspond to the masking complexes were formed from the metal ion and the extracting agent. WAGGFNER AND STOUGHTON[13] in 1952 used an extraction technique to study the complexes formed between thorium(IV) and halide ions. The following expression for the extractability is the reciprocal of the one used by WAGGENER AND STOUGHTON

$$E = \frac{(\mathrm{MR}_n)_o}{(\mathrm{M}) + (\mathrm{MX}) + (\mathrm{MX}_2) + (\mathrm{MX}_3) + (\mathrm{MX}_4)} \quad \text{(6)}$$

where MX, MX_2, MX_3, and MX_4 are the masking complexes in the aqueous phase.

McKAVENEY[14] and KRISHEN[15] have made some very extensive studies of the masked extractions of metal ions using acetylacetone as an extracting agent. SCHWEITZER AND HONAKER[6] appear to be the only ones who have made extensive studies of masked extractions using dithizone as an extracting agent. SCHWEITZER AND HONAKER obtained extraction curves (% metal extracted *versus* pH) for zinc dithizonate extractions in cases in which the aqueous phase contained one of several masking agents. SCHWEITZER AND HONAKER observed that masking agents cause the extraction curves to shift to higher pH values. However, they made no quantitative calculations to predict these shifts.

Statement of present problem

In the present work an extensive study was made of the extraction of silver and cadmium dithizonates from aqueous solutions into either carbon tetrachloride or chloroform containing dithizone. The concentration of dithizone in the organic solvent, $(HD)_o$, was in large excess of the concentration of metal ion in the aqueous phase. In many of the extractions the aqueous phase contained one of several masking agents. Some extractions were made without masking agent being present. In most experiments it was possible to obtain the typical S-shaped extraction curves of pH *versus* % metal extracted. From these curves the $pH_{\frac{1}{2}}$ values were obtained. These $pH_{\frac{1}{2}}$ values are the principal data given in this paper.

Equations used to treat data

It was found that for the non-masked extractions either equation (2) or equation (5) could be used to treat the data. For the treatment of the data from the masked extractions an equation was used which is a modification of equations developed by others[12,13].

By employing the stability constants of the masking complexes, equation (6) may be modified to give

$$E = \frac{(MR_n)_o}{(M) + K_1(M)(X) + K_2(M)(X)^2 + K_3(M)(X)^3 + K_4(M)(X)^4} \quad \ldots\ldots (7)$$

By writing the extractability as in equations (6) and (7) one makes the following assumptions: that no hydrolysis of the metal ion takes place, that no polymeric species are formed, that no mixed complexes are formed, that any complexes in the aqueous phase between M and R are formed to an insignificant amount, that the only significant specie in the organic phase is MR_n, that the concentration of the specie which does the masking is independent of the pH, and that the maximum number of masking ligands attached to the metal ion is four. By dividing the numerator and denominator of equation (7) by $(MR_n)_o$ and factoring (M) from the denominator one obtains

$$E = \frac{1}{\dfrac{(M)}{(MR_n)_o}\left[1 + K_1(X) + K_2(X)^2 + K_3(X)^3 + K_4(X)^4\right]} \quad \ldots\ldots (8)$$

It can be shown that

$$\frac{(M)}{(MR_n)_o} = \frac{(H)^n}{K(HR)_o^n} \quad \ldots\ldots (9)$$

so that

$$E = \frac{1}{\dfrac{(\mathrm{H})^n}{K(\mathrm{HR})_o^n}\left[1 + K_1(\mathrm{X}) + K_2(\mathrm{X})^2 + K_3(\mathrm{X})^3 + K_4(\mathrm{X})^4\right]} \quad \ldots\ldots \quad (10)$$

By making the definitions

$$F = \sum_{i=0}^{4} K_i(\mathrm{X})^i, \text{ and } K_0 = 1 \quad \ldots\ldots \quad (11)$$

one may write

$$E = \frac{K(\mathrm{HR})_o^n}{(\mathrm{H})^n F} \quad \ldots\ldots \quad (12)$$

If the logarithm of equation (12) is taken there results

$$\log E = \log K + n\log(\mathrm{HR})_o + n\mathrm{pH} - \log F \quad \ldots\ldots \quad (13)$$

At 50% extraction equation (13) transforms to

$$0 = \log K + n\log(\mathrm{HR})_o + n\mathrm{pH}_{\frac{1}{2}} - \log F \quad \ldots\ldots \quad (14)$$

Equation (14) is important from three aspects. If the quantities F, n, and $(\mathrm{HR})_o$ are known for an extraction, one may with a knowledge of the value of either one of the terms K or $\mathrm{pH}_{\frac{1}{2}}$, calculate the other. The possibility of determining the stability constants of the masking complexes also presents itself.

EXPERIMENTAL PROCEDURES

Chemicals and apparatus

The water used to prepare solutions was purified with a column of Amberlite MB-3 resin. All glass apparatus was cleaned by washing with cleaning solution, tap water, distilled water, and then demineralized water. All chemicals were U. S. P. grade or better. Salts which contained heavy metals were purified by extracting their solutions with chloroform solutions of dithizone. Some chloroform was recovered and purified by a procedure similar to that of BIDDLE[16]. The dithizone which was Eastman White Label Grade was purified by the procedure given by WELCHER[17].

All pH measurements were made with a Beckman Model H-2 pH meter which was standardized as needed against buffers having pH values of 7.00 and 4.00. The former buffer was used in cases in which the solutions to be measured had a pH above 5.0; the latter was used for measurements below a pH of 5.0. A Tracerlab 1000 Scaler fitted with a GM tube was used to make all radioactivity measurements. Samples were stirred with a battery of magnetic stirrers mounted under a constant-temperature bath which controlled the temperature at 30° ± 0.5°.

Procedures

^{115}Cd and ^{110}Ag were used to measure the per cent of the metal extracted into the organic phase. These nuclides were obtained from the Oak Ridge National Laboratory as nitrates in solution. Both nuclides were of a high specific activity. The procedure used in the experiments was to equilibrate 10-ml portions of aqueous solution of the metal ion with 10-ml portions of the organic phase containing dithizone. The pH of the aqueous phase had been previously adjusted to approximately the desired value. It was possible to equilibrate 12 samples simultaneously and thereby cover a desired pH range. After stirring for two hours the solutions were allowed to stand for 2 h at which time a 100-lambda sample was taken from each phase, placed on a planchet, dried, and counted with the Tracerlab counter. After background counts were subtracted the counts obtained were used to calculate extractabilities and per cent extractions. In all silver extractions the initial concentration of silver in the aqueous phase was approximately $1 \cdot 10^{-7}$ M. In the cadmium extractions an initial concentration of cadmium ion of approximately $7 \cdot 10^{-5}$ M in the aqueous phase was used.

RESULTS

Cadmium extractions

Chloride, bromide and iodide ions were used as masking agents for the extractions of cadmium dithizonate into chloroform. The non-masked extractions were carried out using an aqueous solution containing the perchlorate ion. Data from the non-masked extractions were used to calculate the extraction constant, K, by the use of equation (5). After obtaining a value for K, it was possible to calculate values of $pH_{\frac{1}{2}}$ for the masked extractions by employing equation (14). To make these calculations, it was first necessary to obtain values of the stability constants for the complexes formed between the cadmium ion and the anions of the masking agents. The results of these calculations are shown in Table I along with the data necessary to make the calculations and values of $pH_{\frac{1}{2}}$ which were obtained experimentally. The value of the stability constants of the masking complexes along with the literature sources from which the values were taken are included in Table I. The extraction curves for the cadmium extractions had slopes at 50% extraction which were in good agreement with the value 115% cadmium extracted per pH unit which is the theoretically predicted slope for the extraction of a divalent metal.

TABLE I

RESULTS OF EXTRACTION STUDIES WITH CADMIUM

Initial $(HD)_o$	*Composition of aqueous phase*	*Observed $pH_{\frac{1}{2}}$*	*Calculated*			*Stability constants masking complexes*	*Ref.*
			$pH_{\frac{1}{2}}$	*K*	*log K*		
$5 \cdot 10^{-3}$	$HClO_4$, 0.1 *M* $NaClO_4$	2.0		4	0.6		
$2 \cdot 10^{-3}$	$HClO_4$, 0.1 *M* $NaClO_4$	2.5		3	0.5		
$2 \cdot 10^{-3}$	$HClO_4$, 1.0 *M* $NaClO_4$	2.1		10	1.0		
$5 \cdot 10^{-3}$	$HClO_4$, 0.1 *M* KCl	2.4	2.4			$K_1 = 30$, $K_2 = 200$ $K_3 = 300$	18
$2 \cdot 10^{-3}$	$HClO_4$, 0.1 *M* KCl	3.5	3.2			Same as above	18
$5 \cdot 10^{-3}$	$HClO_4$, 0.1 *M* KI	2.2	3.3			$K_1 = 2 \cdot 10^2$, $K_2 = 8 \cdot 10^3$ $K_3 = 1 \cdot 10^5$, $K_4 = 1 \cdot 10^6$	19
$2 \cdot 10^{-3}$	$HClO_4$, 0.1 *M* KBr	3.0	3.2			$K_1 = 2 \cdot 10^2$, $K_2 = 1 \cdot 10^3$ $K_3 = 3 \cdot 10^3$, $K_4 = 1 \cdot 10^4$	20
$2 \cdot 10^{-3}$	$HClO_4$, 1.0 *M* KBr	4.1	4.3			Same as above	20

TABLE II

RESULTS OF NON-MASKED EXTRACTION STUDIES WITH SILVER

$HClO_4$ molarity	*E*	*$K \cdot 10^{-5}$*	*log K*
1.0	6.2	6	5.8
1.7	3.4	6	5.8
2.9	1.4	4	5.6
3.4	0.9	3	5.5
4.4	0.5	2	5.3
6.0	0.2	1	5.0

Silver extractions

It was not possible to obtain extraction curves for the non-masked silver dithizonate extractions due to the fact that silver extracts at such high acid concentrations. However, some extractions were made into chloroform at know acid concentrations, and the results were used to calculate the extraction constant with the aid of equation (2). Table II gives the data and calculated values of the extraction constant for these systems.

It was found that a number of masking agents would shift the extraction curves of silver to pH values high enough so that extraction curves could be obtained. From these curves pH$_{1/2}$ values were obtained. By the use of equation (14) pH$_{1/2}$ values for extractions into chloroform were calculated for the extractions and compared with the experimental values. For the extractions into chloroform a value of the extraction constant of $6 \cdot 10^5$ as determined from the non-masked extractions was used to calculate pH$_{1/2}$ values. Three extraction curves were obtained for extractions into carbon tetrachloride. Since non-masked extractions were not made into carbon tetrachloride, a value of the extraction constant was not available. Therefore the values of pH$_{1/2}$ from the masked extractions were used to calculate a value for the extraction constant. The data and calculated results for the silver extractions are given in Table III along with the values for the stability constants of the masking complexes and the references from which the values of the constants were taken. All extraction curves for silver extractions had slopes at 50% extraction which were in good agreement with the value of 57% metal extracted per pH unit which is predicted for monovalent metal ions.

Extractions at 30° of silver dithizonate into chloroform were carried out for cases in which the aqueous phase contained one of the following substances: 1.0 *N* acetic acid, 0.1 *M* tartaric acid, 0.1 *M* citric acid, 0.1 *M* glycine, $1 \cdot 10^{-3}$ *M* ethylenediaminetetraacetic acid, $1 \cdot 10^{-3}$ *M* nitrilotriacetic acid, and 0.5 *M* sulfuric acid. No masking effect was found for any of these substances.

Enough data were obtained for extractions from potassium bromide solutions so that values for the stability constants of the silver-bromide complexes were obtained. For the systems which had a potassium bromide concentration of 0.01, 0.05, 0.1, and 0.2 molar Table III gives pH$_{1/2}$ values of 2.6, 4.0, 2.8, and 3.8 respectively for these data are for the systems which had an ionic strength of approximately 0.2 *M*. By the use of these data, the corresponding concentrations of dithizone, and equation (14) four simultaneous equations were written and solved for the values of K_1, K_2, K_3 and K_4. The values obtained for these constants are respectively $3 \cdot 10^4$, $3 \cdot 10^7$, $6 \cdot 10^7$, and $2 \cdot 10^9$.

DISCUSSION

The usual approach by previous investigators to the theoretical aspects of extraction studies such as this one has been to test the extraction technique as a method for determining stability constants of masking complexes. In this work the principal aim was to take values of the stability constants of complexes which could be found in the literature and predict at what pH extraction could be effected. Of all the previous extraction studies that have been made, the authors know of none which has approached the problem in this manner.

It can be seen from Tables I and III that a good degree of succes has been realized

TABLE III

DATA AND CALCULATED QUANTITIES FOR SILVER EXTRACTIONS

Organic phase	Initial $(HD)_0$	Composition of aqueous phase	Observed $pH_{\frac{1}{2}}$	Calculated			Stability constants masking complexes	Ref.
				$pH_{\frac{1}{2}}$	$K \cdot 10^{-5}$	log K		
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.1 M KCl	2.4	2.1			$K_1 = 7 \cdot 10^2$, $K_2 = 1 \cdot 10^4$ $K_3 = 1 \cdot 10^5$, $K_4 = 8 \cdot 10^5$	21
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.2 M KCl	3.1	2.8			Same as above	21
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.01 M KBr	2.9	2.3			$K_1 = 1 \cdot 10^4$, $K_2 = 1 \cdot 10^7$ $K_3 = 9 \cdot 10^7$, $K_4 = 8 \cdot 10^8$	22
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.01 M KBr, 0.2 M $NaClO_4$	2.6	2.3			Same as above	22
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.05 M KBr	4.1	3.8			Same as above	22
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.05 M KBr, 0.15 M $NaClO_4$	4.0	3.8			Same as above	22
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.08 M KBr, 0.12 M $NaClO_4$	4.7	4.3			Same as above	22
$CHCl_3$	$5 \cdot 10^{-4}$	$HClO_4$, 0.1 M KBr	2.9	2.9			Same as above	22
$CHCl_3$	$5 \cdot 10^{-4}$	$HClO_4$, 0.1 M KBr, 0.1 M $NaClO_4$	2.8	2.8			Same as above	22
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.1 M KBr	5.0	4.6			Same as above	22
$CHCl_3$	$5 \cdot 10^{-4}$	$HClO_4$, 0.2 M KBr	3.8	4.4			Same as above	22
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.01 M NaSCN	3.5	3.4			$K_1 = 4 \cdot 10^4$, $K_2 = 1 \cdot 10^8$ $K_3 = 4 \cdot 10^9$, $K_4 = 3 \cdot 10^{10}$	23
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.05 M NaSCN	5.4	5.1			Same as above	23
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, 0.1 M NaSCN	6.2	6.1			Same as above	23
$CHCl_3$	$5 \cdot 10^{-4}$	$HClO_4$, 0.1 M NaSCN	3.7	4.4			Same as above	23
$CHCl_3$	$2 \cdot 10^{-3}$	$HClO_4$, 0.2 M NaSCN	4.1	4.8			Same as above	23
$CHCl_3$	$1 \cdot 10^{-5}$	$HClO_4$, $1 \cdot 10^{-5}$ M, $Na_2S_2O_3$	2.6	2.7			$K_2 = 3 \cdot 10^{13}$, $K_3 = 1 \cdot 10^{14}$	24,25
CCl_4	$1 \cdot 10^{-5}$	$HClO_4$, 0.1 M KCl	1.3		40	6.6	Same as in other chloride extractions	21
CCl_4	$1 \cdot 10^{-5}$	$HClO_4$, 0.2 M KCl	1.9		50	6.7	Same as above	21
CCl_4	$5 \cdot 10^{-5}$	$HClO_4$, 0.1 M KBr	3.1		30	6.5	Same as in other bromide extractions	22

in predicting the pH of 50% extraction for most of the experiments. Since the extraction curves had the shape which was predicted theoretically, it would be as simple a matter to calculate any other pH on the curves as it is to calculate the pH corresponding to 50% extraction.

In the case of extractions of cadmium dithizonate from potassium iodide solutions the calculated and observed values for the pH$_{\frac{1}{2}}$ did not agree. It was thought that possibly a complex between the cadmium ion and the iodide ion such as CdI_2 was extracted into the non-aqueous phase. However, this possibility was not tested experimentally. In the case of two extraction curves for extractions of silver dithizonate from sodium thiocynate solutions, the agreement between calculated and observed values of pH$_{\frac{1}{2}}$ was not as close as expected (see Table III). The difference between the calculated and the observed pH$_{\frac{1}{2}}$ for both of these curves was found to be 0.7 pH unit. It was first thought that equilibrium had not been established for these systems. However, when much effort was made to insure that equilibrium was obtained this difference was still obtained. It should be mentioned that for most of the extractions of silver from sodium thiocyanate solutions a fairly large spread was obtained for the points making up the extraction curve, and quite a large number of extractions were necessary in order to determine the position of the extraction curves. The authors were unable to explain either of these observations for these extractions.

The values of the stability constants of the complexes between the silver ion and the bromide ions are in quite good agreement with those reported in the literature. However, it is difficult to obtain for most systems enough extraction data of sufficient accuracy to permit the determination of all of the constants by solving four equations simultaneously. Other methods[12] of a more graphical nature probably would be better suited in general for the determination of these constants.

The value $3 \cdot 10^6$ for the extraction constants which was determined for silver dithizonate extractions into carbon tetrachloride is not in agreement with a value of $4 \cdot 10^7$ previously reported by TREMILLON[27]. However TREMILLON worked at a temperature of 18° whereas this work was carried out at 30°. Some work has been completed here at this laboratory in which the effect of temperature variation on silver dithizonate extractions was observed. This work tends to show that allowing for the temperature difference the constant determined in this research and the value given by TREMILLON are in fairly close agreement. Also the effect of a change of solvent has been investigated and along with the results of some work dealing with the effects of temperature variation will be reported at a later date.

SUMMARY

An extensive study was made of the solvent extraction of cadmium and silver dithizonates into chloroform. A few extractions of silver dithizonate were made into carbon tetrachloride. In most cases extraction curves of pH *versus* % metal extracted were obtained and reported in terms of the pH of 50% extraction. The shift of the extraction curves to higher pH values due to the effect of ions in the aqueous phase which complex with the cadmium or silver ions was investigated. An equation was developed which would predict the pH of 50% extraction for the extraction from the solutions containing these complexing ions. The effects of chloride, bromide and iodide ions on the extraction of cadmium and the effects of chloride, bromide, iodide, thiocyanate and thiosulfate ions on the extraction of silver. Extraction constants for the various extractions were determined.

RÉSUMÉ

Une étude approfondie a été effectuée sur l'extraction par un solvent des dithizonates de cadmium et d'argent. On a déterminé les constantes d'extraction dans divers cas et examiné l'influence d'anions complexants.

ZUSAMMENFASSUNG

Es wurde der Verlauf der Extraktion der Dithizonate des Cadmiums und Silbers mit Chloroform in Abhängigkeit vom pH der Lösung und der Einfluss komplexbildender Anionen und Halogeniden auf die Extraktion untersucht.

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SPECTROPHOTOMETRIC DETERMINATION OF THE RARE EARTHS YTTRIUM AND CERIUM BY BROMOPYROGALLOL RED

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INTRODUCTION

The use of bromopyrogallol red as a chromogenic reagent for the spectrophotometric determination of the rare earth type elements was suggested by its use as an indicator in certain rare earth titrations[1]. This reagent forms coloured, sparingly soluble complexes with many metal ions; with the rare earths, yttrium and cerous cerium, blue to violet-blue complexes are formed in solutions of pH greater than about 4.5. The bromopyrogallol red also exhibits acid–base indicator properties, being orange yellow in strong acid solution, claret red in nearly neutral solution and blue in alkaline solution.

The procedure to be described is suitable for pure solutions of the rare earths, yttrium and cerous cerium *e.g.* after preliminary precipitation as fluoride followed by separation on an ion-exchange column. The complex is quite stable under the conditions specified and the Beer Lambert law is obeyed at least between the range of concentration 0.5 to 4.0 p.p.m. of metal ion.

EXPERIMENTAL WORK

Preliminary experiments showed that the pH value of the solution should be maintained at an optimum value within the range 5.0–7.0. The addition of sodium acetate was found to meet this requirement, being added to stabilize the final acidity of the solution.

The colour development of the bromopyrogallol red–rare earth complex was also found to be slow at room temperature and to obtain stable conditions it was necessary to heat the sample solution for 10 min in a water bath at 80–90°.

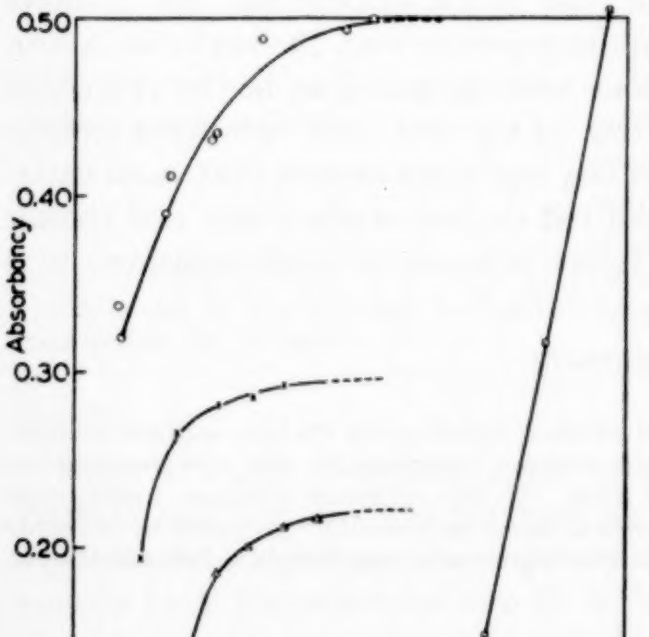

Fig. 1. Showing the effect of pH on the colour development of the bromopyrogallol red-rare earth complex. o = gadolinium and terbium curve, × = europium and neodymium curve, Δ = yttrium curve, □ = bromopyrogallol red solution.

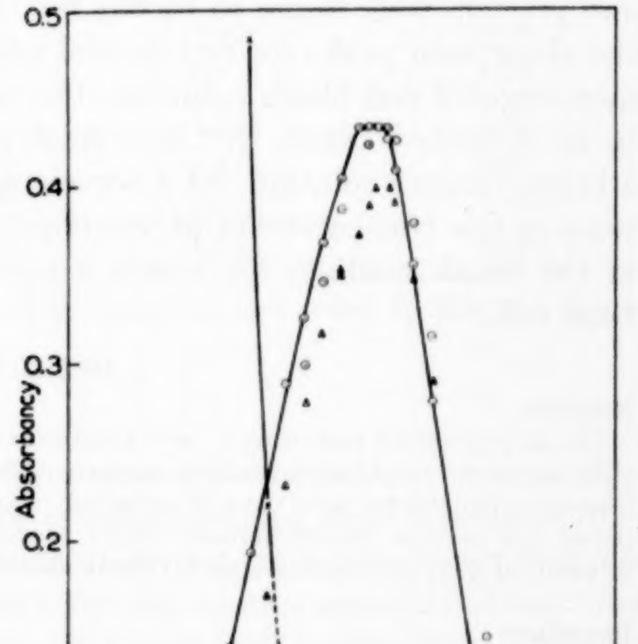

Fig. 2. Showing the absorption curves for neodymium and cerium. o = neodymium curve, Δ = cerium curve, × = bromopyrogallol red solution at pH 6.5.

Effect of pH on colour development

Individual portions, each containing 20–50 μg of rare earth in dilute acid solution were adjusted to about 15 ml volume with water and 2 ml 0.05% w/v bromopyrogallol red in 50% alcohol were added, followed by the dropwise addition of 5% w/v sodium bicarbonate solution until a blue colour appeared at about pH 5. This colour was then discharged by the careful addition of 0.2 *N* hydrochloric acid, 0.10 ml of 55% w/v sodium acetate was added and the acidity adjusted with dilute hydrochloric acid or sodium hydroxide. The solution was then diluted to about 20 ml volume, heated in a water bath for 10 min, and, after cooling, transferred to a volumetric flask and diluted to a final volume of 25 ml. The absorbancy of the solution was then measured in a 1-cm cell using a Unicam SP600 spectrophotometer, at a wavelength of 665 mμ. The results are presented in Fig. 1 together with the absorbancy values for a bromopyrogallol red solution, at various acidities, without any rare earth present.

The optimum pH range for complex formation is 6.0–7.5. Above pH 7.5 the reagent blank will increase and also make the final pH value of the solution difficult to stabilize. Under the conditions of the method to be described a final pH of 6.4–6.5 is to be expected.

Absorption spectra

The absorption peaks for neodymium, europium, samarium, gadolinium, terbium and yttrium were found to be 665 mμ, whilst that for Ce was 675 mμ. Fig. 2 shows the absorption peaks for cerium and neodymium together with the curve for a bromopyrogallol red blank solution. The solutions were prepared as in the procedure to be described below, giving a final pH value of 6.5 and were measured against a blank reagent solution. At a wavelength of 665 mμ it can be seen that small variations in the concentration of bromopyrogallol red do not produce any real change in the blank reading, for which a typical figure is 0.005 to 0.010 measured in a 1-cm cell.

DETAILED METHOD

Reagents

Bromopyrogallol red: 0.05% w/v solution in 50% alcohol (indefinitely stable), sodium acetate: 55% aqueous solution of sodium acetate trihydrate, sodium bicarbonate: 5% w/v aqueous solution, hydrochloric acid: 0.2 *N* solution, ascorbic acid: 1% w/v aqueous solution, freshly prepared (for cerium determinations only), standard solutions of rare earths: prepared by accurate dilution of gravimetrically standardized solutions of the "Specpure" nitrates in dilute nitric acid.

Procedure

Rare earths and yttrium: Transfer the sample, containing 15–35 μg of yttrium or 20–50 μg of rare earth, in dilute acid solution, to a 25-ml measuring flask (Note 1). Dilute to about 15–16 ml with water. Add 2.0 ml of the bromopyrogallol red reagent and then 5% sodium bicarbonate solution, dropwise, until one drop produces a permanent blue colour. Wash down the neck of the flask with water and then add 0.2 *N* hydrochloric acid, dropwise, until the blue colour is discharged, leaving a clear red solution. Add 0.50 ml of 55% sodium acetate solution, and stand the flask in a hot water bath (80–90°) for 10 min. Cool, and dilute to the mark with water. (Note 2). Measure the absorbancy of the solution against water in 1-cm cells at 665 mμ. Carry out similar determinations on accurately measured portions of the diluted standard solutions. The Beer-Lambert law is obeyed.

Plot a calibration curve of absorbancy against concentration of rare earth. Obtain a blank reading from the interception of the calibration line with the absorbancy axis. A figure of approximately +0.005 is to be expected.

Cerium: As for rare earths and yttrium above except that 0.2 ml of 1% ascorbic acid is added before the addition of the bromopyrogallol red, to ensure reduction of any ceric cerium, and the final solution is measured at 675 mμ.

TABLE I

	Weight of solution (g)	*Absorbancy*[a]	*Absorbancy per gram of solution*
Neodymium (234.8 μg Nd/g)	0.0634	0.202	3.19
	0.0976	0.312	3.20
	0.1354	0.428	3.16
	0.1834	0.580	3.17
Gadolinium (537.0 μg Gd/g)	0.0527	0.355	6.74
	0.0742	0.490	6.61
	0.0758	0.500	6.60
	0.1057	0.705	6.67
Terbium (not standardized. Approx. 235 μg/g Tb)	0.1102	0.317	2.88
	0.1860	0.540	2.90
	0.2607	0.755	2.90
	0.3744	1.08	2.88
Yttrium (99.50 μg Y/g)	0.1159	0.255	2.20
	0.1313	0.288	2.19
	0.2248	0.490	2.18
	0.2642	0.576	2.18
	0.3386	0.738	2.18
	0.3707	0.813	2.19
Cerium (193.6 μg Ce/g)	0.0852	0.263	3.09
	0.1032	0.319	3.09
	0.1987	0.614	3.09
	0.3401	1.04	3.06

[a] A blank of +0.005 was subtracted from the absorbancy against water to give the figures recorded in this column.

Results

Table I shows a typical series of standardisations on individual rare earths, yttrium and cerium. The portions for these standardisations were dispensed from a polythene weight pipette, capacity approximately 7 g, of a type described previously by J. HERRINGTON AND D. G. VALLIS[2]. By this means, amounts of the order of 0.1 g were dispensed using a damped balance with automatic loading for all weights and with a precision of 0.2 mg. This method of dispensing small amounts of liquid has the advantage of quickness and is not influenced by temperature effects on the volume of the solutions concerned. The results are therefore quoted as absorbancies per g of solution. Results obtained on gravimetrically standardized solutions show that under the conditions of the above procedures, 20 μg of Nd give an absorbancy of 0.271, 20 μg of Y give an absorbancy of 0.439, 20 μg of Gd give an absorbancy of 0.248 and 20 μg of Ce give an absorbancy of 0.319.

Interfering ions

These procedures have been developed to deal with purified, separated solutions obtained from ion-exchange columns. The following ions are known to give complexes at the pH of the determinations: Fe^{+2}, Cu^{+2}, Pb^{+2}, Be^{+2}, Zn^{+2}, Co^{+2}, VO_4^{-2}, Mg^{+2} (see Table II). Fe^{+3} and peroxide decolourize the solution.

TABLE II

THE INFLUENCE OF IMPURITIES ON THE COLOUR DEVELOPMENT OF THE NEODYMIUM–BROMOPYROGALLOL RED COMPLEX

Element	*Amount of impurity element added* μg	*Amount of neodymium added* μg	*Amount of neodymium found* μg
Iron (as Fe^{+2})	150	53	32
Copper (as Cu^{+2})	300	53	44
Lead (as Pb^{+2})	200	53	58
Beryllium (as Be^{+2})	200	53	53
Beryllium (as Be^{+2})	1000	53	precipitated
Zinc (as Zn^{+2})	250	53	precipitated
Cobalt (as Co^{+2})	100	53	precipitated
Vanadium (as VO_4^{-2})	100	53	46
Magnesium (as Mg^{+2})	500	53	52
Magnesium (as Mg^{+2})	3000	53	precipitated

Notes

1. (a) Excessive amounts of acid are best removed by evaporation of the sample to dryness and dissolution in the minimum of warm 0.5 *N* hydrochloric acid.
   (b) It is more convenient to place the sample in a volumetric flask in the first stage of the experiment rather than to transfer the solution at a later stage. After heating a volumetric flask to a temperature of 100° in a water bath and allowing to cool, there is no detectable change in the calibration.
2. At this stage in the procedure the pH will be 6.4–6.5 by virtue of the sodium acetate solution added.

SUMMARY

A method is described for the spectrophotometric determination of microgram quantities of rare earths, yttrium and cerous cerium ions, using the colour of the complexes formed with bromopyrogallol red. The procedure has been applied to pure solutions containing 10–50 μg of the element.

RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique des terres rares, de l'yttrium et du cérium(III). On utilise le rouge de bromopyrogallol comme réactif.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur spektrophotometrischen Bestimmung der seltenen Erden, des Yttriums und Cer(III) mit Hilfe von Bromopyrogallolrot.

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COLORIMETRIC DETERMINATION OF SILICON IN THE PRESENCE OF PHOSPHORUS

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During the investigation leading to the colorimetric determination of silicon in biological materials as molybdenum blue, various methods for the removal of the interference from phosphorus were investigated. Complexing agents such as oxalic[1,2] or citric acid[2,3] were used to bleach the interfering phosphomolybdate while leaving the silicomolybdate unaffected. This method is successful when only small amounts of phosphate are present to interfere, but in the presence of high concentrations of phosphate such as are found in human and rat urine, the method is not applicable unless the urine is diluted considerably. This is undesirable, for when silicate is present in only small amounts it might then escape detection and determination.

We have considered the possibility of removing most of the phosphate by a controlled precipitation method, and eliminating the small amount of remaining phosphate by solvent extraction of the heteropoly acid of phosphorus.

HURE AND ORTIS[4] have reported the extraction of phosphomolybdate from a mixture of the heteropoly acids of silicon and phosphorus by solvent extraction with ethyl acetate. WALDEN AND MELLON[5] have summarized the data on solvent extraction of phosphorus, silicon, arsenic and germanium. DE SESA AND ROGERS[6] have briefly reported the application of this solvent extraction technique to the determination of silicon and phosphorus in the presence of each other. Silicon was determined in their experiments by measurement of the total absorbance of the yellow molybdate at 332 mμ, extraction of the phosphate by isoamyl acetate and measuring the absorbance of the organic phase at 330 mμ. The silicon content was given by correcting total absorbance in the aqueous phase for phosphorus, using the previously determined absorbance index of phosphomolybdate in the aqueous phase.

Since we were interested in the determination of silicon only, the above method of determination was unnecessarily time consuming. After solvent extraction of the phosphomolybdate, silicon in the aqueous layer was determined by reduction of the silicomolybdate to molybdenum blue with sodium sulphite solution. Using this method of investigation, we have studied the efficiency of extraction of the heteropoly acids of phosphorus and silicon by several solvents. Selective solvent extraction of phosphomolybdate in the presence of silicomolybdate has been studied in detail, and a reliable and accurate method of determination of silicon in the presence of phosphorus is reported.

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EXPERIMENTAL

Reagents

Distilled water was used throughout. A stock solution of phosphate was prepared by dissolving 0.500 g of disodium hydrogen phosphate in water and diluting to 100 ml. Further solutions of phosphate were prepared by appropriate dilution from the stock solution.

Solutions of soluble silica were prepared by fusing 10.0 mg of finely divided quartz, 0.5 g of powdered sucrose and 1.5 g of sodium peroxide in a Parr-Bomb, and dissolving the cold melt in 100 ml of water, in a polythene beaker. Further standard solutions of silicate were prepared by appropriate dilution.

Phosphate determination

Phosphate was determined by the method of KING[7]. This involved the formation of phosphomolybdate and reduction of this complex by 1-amino-2-naphthol-4-sulphonic acid.

Silicon determination

Silicon was determined colorimetrically by a modification of the method of DIENERT AND WALDENBULKE[8]. The yellow silicomolybdate was reduced with sodium sulphite solution (30%) to molybdenum blue and the optical density was measured in a spectrophotometer at 690 mμ. The following reagents were added (in the order stated): 2.0 ml standard silicate solution (0.02 mg to 0.10 mg), 2.0 ml *N* hydrochloric acid, 4.0 ml ammonium molybdate solution (5%) (tetrahydrate), 4.0 ml sodium sulphite solution (30%) (heptahydrate).

For the blank determination the same volume of each reagent was used (2 ml water replaced the standard silicate solution) and this was used as a compensating solution. This method of determination had an accuracy of 98.9%[9].

Solvent extraction procedure

Into a 50-ml separating funnel was pipetted 2 ml of the test solution. During shaking of the funnel, 2 ml of *N* hydrochloric acid was added, then 4 ml of ammonium molybdate solution (5%) and the shaking was continued for a further 3 min. This solution had a pH of 1.0. It was then extracted once with 20 ml of an organic solvent for 30 sec. The aqueous phase was separated and 4 ml of sodium sulphite solution (30%) was added. The resulting solution was allowed to stand for 25 min for maximum colour to develop, and its optical density was then measured at 690 mμ, against the extracted blank.

TABLE I

SOLVENT EXTRACTION OF HETEROPOLY ACIDS OF PHOSPHORUS AND SILICON

Solvent	*Initial phosphate concentration 500 µg/2 ml*	*Initial silicon concentration 57 µg/2 ml*
	Phosphate found in aqueous phase after solvent extraction µg	*Silica found in aqueous phase after solvent extraction* µg
Ethyl acetate	< 5	57
n-propyl acetate	< 5	57
isopropyl acetate	< 5	55
n-butyl acetate	< 5	57
isobutyl acetate	< 5	56
n-amyl acetate	500	56
isoamyl acetate	40	57
diethyl ether	250	57
dibutyl ether	350	56
n-hexyl butyrate	270	57

RESULTS

In Table I is recorded the result of a preliminary study on the extraction of phospho- and silicomolybdate by various solvents. Phosphomolybdate was removed to some extent by all the solvents tested, except *n*-amyl acetate, but complete extraction within the limits of the experiment, was obtained with only ethyl acetate, *n*-propyl acetate, isopropyl acetate, *n*-butyl acetate and isobutyl acetate. 92% of the phosphomolybdate was extracted by isoamyl acetate but *n*-amyl acetate gave no extraction. Silicomolybdate was not extracted by any of the solvents.

TABLE II

EXTRACTION STUDIES WITH ETHYL ACETATE AND ISOAMYL ACETATE
REMOVAL OF PHOSPHOMOLYBDATE

Phosphate present before extraction µg	*Phosphate found in aqueous phase after single ethyl acetate extraction* µg	*Phosphate found in aqueous phase after single isoamyl acetate extraction* µg	*Phosphate found in aqueous phase after double isoamyl acetate extraction* µg
200	< 5	15	< 5
500	< 5	40	11
750	< 5	60	20
1000	< 5	80	25
1500	8	115	25

The results in Table II show that the efficiency of extraction of phosphomolybdate by ethyl acetate was actually 100%, whereas only about 92% of the phosphomolybdate was removed from the aqueous phase when isoamyl acetate was used as solvent. On the other hand, silicomolybdate was not extracted by either ethyl acetate or isoamyl acetate, virtually 100% recovery of silica was obtained in the aqueous phase after solvent extraction by both reagents as shown in Table III.

TABLE III

EFFECT OF ETHYL ACETATE AND ISOAMYL ACETATE EXTRACTION ON SILICOMOLYBDATE[a]

Silica present before extraction µg	*Silica found after single ethyl acetate extraction* µg	*Silica found after single isoamyl acetate extraction* µg
38	35	38
64	64	64
70	66	69
135	135	135
157	157	160

[a] Solutions of soluble silica were treated with acid molybdate solution and the resulting yellow silicomolybdate solution extracted by the standard procedure.

To complete this study, the colorimetric determination of silica in the presence of phosphate was checked after extraction with ethyl acetate and isoamyl acetate. The results of these experiments, which are recorded in Table IV, demonstrate that after a single extraction with ethyl acetate apparent recoveries of between 100.0 and 103.1% of silica were obtained but single extractions with isoamyl acetate, in similar experiments, gave abnormally high silica recoveries. Double extraction with isoamyl acetate reduced this interference by phosphate but duplicate extraction with this solvent was less efficient than a single ethyl acetate extraction for the removal of phosphomolybdate. Double extraction with ethyl acetate was not used because the additional extraction might be expected to cause new errors. This method of silicon determination, employing ethyl acetate for the removal of phosphomolybdate, gave a mean error of +2.1% in 8 determinations (Table V).

TABLE IV

RECOVERY OF SILICA IN THE PRESENCE OF PHOSPHATE[a]

Silica present before extraction µg	*Silica found after single ethyl acetate extraction µg*	*Apparent recovery %*	*Silica found after single isoamyl acetate extraction µg*	*Apparent recovery %*	*Silica found after double isoamyl acetate extraction µg*	*Apparent recovery %*
60	61	101.7	100	166.7	72	120.0
50	50	100.0	82	164.0	61	122.0
65	67	103.1	106	163.1	78	120.0
58	58	100.0	100	172.4	68	117.2

[a] To solutions of soluble silica were added 2 ml sodium phosphate solution containing 500 µg/ml. The phosphomolybdate was removed by solvent extraction and silica was determined in the aqueous phase.

TABLE V

ACCURACY OF METHOD OF DETERMINATION[a]

Silicon present before extraction µg	*Silicon found after extraction µg*	*% error*
61	62	+ 1.7
52	52	0.0
36	38	+ 5.6
14	14	0.0
132	135	+ 2.3
58	58	0.0
26	27	+ 3.8
65	67	+ 3.1
	Mean % error =	2.1 ± 0.7

[a] To solutions of soluble silica were added 2 ml sodium phosphate solution containing 500 µg of sodium phosphate per ml. The phosphomolybdate was removed by single extraction with ethyl acetate and silica was determined in the aqueous phase.

DISCUSSION

In a preliminary study on the selective removal of phosphomolybdate in the presence of silicomolybdate in aqueous solution (pH 1.0) ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, amyl acetate, isoamyl acetate, diethyl ether, dibutyl ether and hexyl butyrate were tested. Although phosphomolybdate was extracted to some extent by all the organic solvents tested (except amyl acetate), ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate and isoamyl acetate were the most efficient.

In a more detailed study of the efficiency of extraction of phospho- and silicomolybdate with ethyl acetate and isoamyl acetate as measured by colorimetric determination of molybdenum blue, ethyl acetate was found to have a much greater efficiency, reducing phosphate interference to tolerance level. Thus, accurate and reproducible colorimetric determinations of silicon were obtained using solutions of silicate containing 1000 µg phosphate, this being about the highest permissible concentration of phosphate which will not cause precipitation of insoluble phosphomolybdate.

ACKNOWLEDGEMENT

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SUMMARY

An accurate and reliable colorimetric method of silicon determination in the presence of phosphorus is reported. The method involves the selective extraction of phosphomolybdate with ethyl acetate and determination of the aqueous phase after reduction to molybdenum blue. Isoamyl acetate extracts phosphomolybdate to a lesser degree than ethyl acetate.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le dosage du silicium en présence de phosphore. Principe: extraction du phosphomolybdate par l'acétate d'éthyle et dosage colorimétrique après réduction de la phase aqueuse en bleu de molybdène.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur colorimetrischen Bestimmung von Silizium in Gegenwart von Phosphor. Phosphormolybdat wird mit Aethylacetat selektiv extrahiert, das Silicomolybdat zu Molybdänblau reduziert und colorimetrisch bestimmt.

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ANALYSIS OF ALLOYS OF TITANIUM, NIOBIUM AND TANTALUM BY ION EXCHANGE

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In connection with studies of the oxidation behaviour of titanium alloys methods were required for the analysis of binary and ternary alloys of titanium, niobium, and tantalum. HAGUE, BROWN AND BRIGHT[1] have shown that titanium and niobium may be separated by ion exchange as chloro-fluoro complexes; niobium and tantalum may be separated similarly[2]. In the present work a method is presented in which titanium, niobium and tantalum are separated by ion exchange in hydrochloric–hydrofluoric acid media. After the separation the metals are determined spectrophotometrically.

EXPERIMENTAL

Preparation of column

The column was prepared from a 90-cm long polyethylene tube with inside diameter 1.1 cm. The bottom of the tube was closed by a polyethylene stopper. A polyethylene tube with inside diameter 0.2 cm was inserted through a hole in the stopper flush with the upper surface of the stopper. The stopper was covered with a cotton plug and the large tube was filled with a 10-cm high layer of 120–200 mesh Amberlite IRA-400 resin.

Solutions

Acid mixture 1: Mix 200 ml of hydrofluoric acid (40%, $d = 1.13$) and 400 ml of hydrochloric acid ($d = 1.19$) and dilute to 1 l with distilled water.
Acid mixture 2: Mix 50 ml of hydrofluoric acid and 250 ml of hydrochloric acid and dilute to 1 l with distilled water.
Acid mixture 3: Mix 750 ml of hydrofluoric acid with 250 ml of hydrochloric acid.

Procedure

Separation. Transfer 100 mg of the alloy to a platinum dish and add 2 ml of sulfuric acid and 2 ml of hydrofluoric acid. Add nitric acid dropwise until the sample has dissolved. Evaporate to fumes of sulfuric acid. Add 15 ml of acid mixture 1 and transfer the solution to the column. The elution of titanium is performed with 100 ml of acid mixture 1 at a flow rate of 2 ml/min. Niobium is then eluted with 100 ml of acid mixture 2. Finally, tantalum is eluted with acid mixture 3. Reject the first 100 ml of this eluate as it will contain no tantalum. Tantalum is quantitatively eluated with the next 300 ml (flow rate 2 ml/min).

Spectrophotometric determination

Titanium and niobium. Transfer the eluates containing titanium and niobium to platinum dishes, add 5 ml of concentrated sulfuric acid and evaporate to fumes. Add 2–3 drops of hydrogen peroxide and again fume to destroy organic matter from the column. Transfer the solutions to 50-ml volumetric flasks. Add 0.5 ml of hydrogen peroxide (30%) and make up to volume with conc. sulfuric acid. Mix thoroughly and read the absorbance at 430 and 365 mμ for titanium and niobium respectively. Alternatively, titanium may be determined as the hydrogen peroxide complex in 6 N sulphuric acid reading the absorption at 410 mμ.

Tantalum. (Reagent solution. Dissolve 50 g of pyrogallol in 150 ml of distilled water. Add 15 ml of sulfuric acid (1 + 9) and dilute to 250 ml in a volumetric flask.)

To the eluate containing tantalum add a few drops of sulfuric acid and evaporate to dryness in a platinum dish. Add 0.5 g potassium hydrogen sulfate and fuse. Cool and add 1 g of ammonium oxalate and 10 ml of water and warm to dissolve the salts. Transfer the solution to a 25-ml volumetric flask and make up to volume with distilled water. Transfer a 5-ml aliquot to another 25-ml volumetric flask, add 0.8 g of ammonium oxalate and 12 ml of reagent solution. Make up to volume with distilled water and read the absorbance at 400 mμ.

DISCUSSION AND RESULTS

Titanium and niobium are easily separable under a wide variety of hydrochloric and hydrofluoric acid concentrations using a large column[1]. In the proposed method a much smaller column is used in order to reduce the volumes of eluting solutions. Separation of titanium and niobium under these conditions was, however, found to be incomplete using the acid mixtures previously investigated[1]. These studies indicated, however, that the elution rate of niobium is decreased by increasing the acid concentrations, whereas the rate of titanium elution is little affected. Accordingly the separation with stronger acid mixtures was investigated. "Acid mixture 1" was found to separate the metals completely. Titanium was quantitatively washed out with 100 ml of the mixture, 150 ml being required before niobium could be detected in the eluate. This was found to be true for samples containing varying amounts of the metals (total = 100 mg).

The elution of tantalum requires a high acid concentration, the most effective acid mixture being 17.3 N HF–3 N HCl[2] (acid mixture 3). Tantalum was quantitatively eluted with 400 ml of this acid mixture using the small column. The following mixtures of concentrated acids: 14 N HF–4.8 N HCl, 19.5 N HF–1.8 N HCl, and 11.5 N HF–6 N HCl were found to require 500, 550, and 550 ml respectively for quantitative elution.

Tantalum can be determined as peroxide in conc. sulfuric acid by a procedure similar to that used for titanium and niobium. But the absorption maximum lies in the ultraviolet region, and high and varying blanks were obtained probably owing to contaminations from the column. The pyrogallol method was therefore preferred.

Some results obtained by analyzing mixtures of standard solutions made from spectrographically pure metals are listed in Table I.

TABLE I

DETERMINATION OF TITANIUM, NIOBIUM AND TANTALUM BY ION EXCHANGE

	mg metal			*mg metal*	
	present	*found*		*present*	*found*
Ti	32.0	32.0	Ti	10.3	10.3
Nb	27.3	27.5	Nb	81.7	82.0
Ta	33.3	33.6	Ta	24.7	25.0
Ti	9.6	9.7	Ti	90.0	—
Nb	15.7	15.8	Nb	1.14	1.17
Ta	73.1	73.2			
			Nb	85.6	85.0
			Ta	12.7	12.7

ACKNOWLEDGEMENT

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SUMMARY

A procedure for the analysis of alloys of titanium, niobium and tantalum is described. After dissolution the metals are separated by ion exchange in hydrochloric–hydrofluoric acid media. Finally the metals are determined spectrophotometrically.

RÉSUMÉ

Une méthode d'analyse est décrite pour les alliages de titane, niobium et tantale. Les métaux sont séparés par échangeur d'ions et dosés finalement par spectrophotométrie.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse der Legierungen von Titan, Niob und Tantal. Die Metalle werden mit einem Ionenaustauscher getrennt und spektrophotometrisch bestimmt.

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THE MICRO-DETERMINATION OF GOLD WITH *p*-DIMETHYLAMINOBENZYLIDENERHODANINE

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INTRODUCTION

An absolute measure of the amount of gold on thin films was required in order to calibrate a secondary optical method of neutron flux measurement. An examination of published methods showed that none could measure amounts of the order of 10 μg to within 1–2%. Thus the *o*-tolidine method[1] was too insensitive in our hands, the dithizone method although sensitive was irreproducible, and the rhodamine B method[2], from the published figures, too inaccurate. The *p*-diethylaminobenzylidenerhodanine method[3] in which a colloidal complex is formed in dilute acid solution was also impossible to reproduce within the required limits. A modification of the method in which the complex is extracted into a non-aqueous phase is described.

EXPERIMENTAL

Extracting solvent and reagent

The dimethylaminobenzylidenerhodanine was purified by dissolving in acetone and partly precipitating with water. An ethanolic solution of the dried product (0.04%, w/v) was used for trial extractions of 5 μg of gold from a dilute hydrochloric acid solution (about 0.12 *N*). Isoamyl acetate was the best extractant amongst chloroform, carbon tetrachloride, isoamyl alcohol, diethyl ether, benzene–chloroform (1 : 3) and isoamyl acetate. It gave the quickest extraction and had the advantages of a low volatility, and a clean separation from the aqueous phase. Most of the colour of the organic phase was caused by the yellow colour of the reagent with a maximum absorption at 455 mμ. The red-orange gold complex could be observed with more dilute solutions of the reagent and had an absorption peak at 510–515 mμ. In order to estimate small amounts of gold accurately the minimum excess of reagent compatible with complete formation of complex is required. The dilute solution of reagent can be made by extracting a portion of the ethanolic solution, diluted with water, into isoamyl acetate, or directly by diluting a stronger solution of rhodanine in isoamyl acetate. On the basis of a 1 : 1 gold-rhodanine complex, 1 ml of a 0.004% solution w/v can complex 30 μg of gold.

SOLUTIONS

Standard gold solutions: A stock solution (500 μg/ml) was prepared by dissolving gold wire in a minimum of aqua regia, evaporating almost to dryness twice with hydrochloric acid and making to a standard volume. The working solution (5 μg/ml) was prepared by dilution immediately before use. Deionized water was used for all solutions.

Constant boiling point hydrochloric acid and iso-amyl acetate: The standard laboratory grade was used without purification.

p-Dimethylaminobenzylidenerhodanine: A dilute solution in isoamyl acetate, 0.0044% (w/v) was prepared as described from a stronger stock solution. The dilute solutions are stable.

PROCEDURE

The gold film was dissolved from its terylene support in a minimum of aqua regia and evaporated almost to dryness in a water bath with some additional hydrochloric acid. The last traces of volatile acid were removed by blowing air over the surface. The residual chlor-auric acid was diluted suitably to a standard volume and an aliquot containing between 4 and 10 μg taken. 0.10 ml ± 0.005 of constant boiling point acid was added and the total volume was adjusted to 5.00 ml; 0.30 ml of rhodanine reagent and 10.0 ml of isoamyl acetate were then added. The container, a test tube stoppered by a B14 cone covered with a "Teflon" cone to prevent solvent leakage, was shaken mechanically for 15 min; the organic layer was then poured through cotton wool directly into a 4-cm absorption cell (volume 10 ml) and the absorption of the gold solution compart with a blank (5.00 ml of water taken through the procedure) at 515 mμ after 5 min.

Effect of acidity

The acidity must be closely controlled because the colour decreases with increasing acidity. The complex is no longer formed when the acidity is greater than 1 *N*.

TABLE I

EFFECT OF ACIDITY ON EXTRACTION OF 4.6 μg OF GOLD

Normality of acid	*log I_0/I*
0.06	0.109
0.12	0.106
0.18	0.083

TABLE II

STABILITY OF AN EXTRACT OF 7.04 μg OF GOLD

Time (minutes)	*log I_0/I*
5	0.159
10	0.159
15	0.155
30	0.152
45	0.148

Effect of time on the coloured complex

The colour fades slowly and should be measured within ten minutes of extraction.

Effect of time on extraction of complex

The time for complete extraction increases with dilution of the reagent. Extraction times should not be prolonged to avoid fading of the colour. Complete extraction under the above conditions is obtained after 10–15 min.

TABLE III

TIME REQUIRED FOR COMPLETE EXTRACTION OF COMPLEX

(5.03 μg gold measured 5 min after extraction)

Extraction time (minutes)	*log I_0/I*
5	0.097
10	0.114
15	0.118
20	0.117

Effect of reagent strength

The range covered may be extended above 10 μg with a stronger reagent solution without further calibration. An excess of reagent should always be present to ensure complete extraction of gold. A 50–100% excess is advised.

Effect of temperature

No effect was observed when the ambient temperature varied from 19–29°.

The average absorbance/μg of gold for solutions whose absorbancy can be measured to 1% (*i.e.* not less than 4 μg) is 0.0231 ± 0.002. The mean deviation is therefore within ± 1% and the maximum deviation within ± 2%. The method is therefore as sensitive as the aqueous method and much more precise.

RESULTS AND DISCUSSION

TABLE IV

CALIBRATION CURVE

Gold (µg)	*log I_0/I*	*log I_0/I/µg*	*Reagent strength*
1.01	0.024	0.023(8)	1 ml ≃ 30 µg gold
2.01	0.047	0.023(4)	
3.02	0.071	0.023(3)	
4.03	0.093, 0.094, 0.094	0.0233	
5.03	0.117, 0.118	0.0234	
6.04	0.139, 0.139, 0.139	0.0230	
7.04	0.159	0.0226	
8.05	0.186	0.0231	1 ml ≃ 60 µg gold
9.06	0.209	0.0231	
10.06	0.233	0.0231	
11.07	0.257	0.0233	
12.07	0.281	0.0232	
14.09	0.321	0.0228	

The composition of the complex is reputed to be the same as that of the silver complex in which the hydrogen of the acidic imino group is replaced by univalent silver. The maximum colour obtained with a particular strength of dilute reagent indicates that only one atom of gold combined with a molecule of rhodanine (*e.g.* a reagent containing 14.4 ± 0.4 µg of rhodanine in 0.30 ml gave a maximum absorbance of 0.222, which from the calibration curve corresponds to 9.6 µg of gold. A 1:1 complex would contain 9.8 ± 0.3 µg). However, it is unlikely that the complex contains aurous gold because the reduction of auric gold would oxidize the rhodanine and the aurous chloride formed could disproportionate. Both phenomena would be expected to give irreproducible colours. The retention of trivalent gold in a complex anion is more probable.

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SUMMARY

Gold can be determined in the range 4–14 µg within 2% by a simple extraction of chlorauric acid in 0.12 *N* hydrochloric acid with a solution of *p*-dimethylaminobenzylidenerhodanine in iso-amyl acetate. A 1 : 1 complex is formed with maximum absorption at 515 mµ.

RÉSUMÉ

Un microdosage de l'or est proposé au moyen de la *p*-diméthylaminobenzylidènerhodanine, avec extraction dans l'acétate d'iso-amyle.

ZUSAMMENFASSUNG

Tetrachlorogoldsäure bildet mit *p*-Dimethylaminobenzyliden-rhodanin einen Komplex, der in Isoamylacetat löslich ist. Diese Reaktion kann zur Bestimmung sehr kleiner Goldmengen nach dem Extraktionsverfahren verwendet werden.

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COLOUR REACTIONS AND PAPER CHROMATOGRAPHIC STUDIES OF YTTRIUM AND ZIRCONIUM

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INTRODUCTION

Many procedures have been reported concerning the determination of yttrium or zirconium after separation by the usual analytical methods. These include spectrometric determinations[1-7], amperometric titrations[8], gravimetric[9-13], volumetric[14], complexometric[15-20], colorimetric[21-25], and other procedures.

This paper presents a detailed account of the colour reactions of yttrium and zirconium with different organic compounds in visible and ultra-violet light, as well as the sensitivity of each reaction for the determination of these elements. Furthermore, some organic solvents are reported which may be used for their separation.

EXPERIMENTAL

Schleicher and Schüll No. 2043a paper (30 cm × 6 cm) was used for the chromatography by the downward elution method. The selected solvent mixtures were allowed to pass first through the paper and then the metal solutions were applied by means of a microapparatus (Desaga Mikrometer-Dosiergerät) after the paper had been dried by air; 0.05 ml of aqueous yttrium chloride or zirconium chloride solutions containing 20–30 µg of the element was used. The spots were dried with hot air, and the paper strip was inserted into the eluting solvent. When the solvent had percolated a sufficient distance down the paper strip, the chromatogram was removed and dried with hot air.

For the quantitative estimation of the sensitivity of each reaction, increasing amounts from 0.5 to 30 µg were plotted on the paper at 2-cm intervals and the lowest positive colour reaction was noted.

Depending on the solubility of the compounds in water or alcohol, 0.1–0.5% w/v aqueous or alcoholic solutions of the reagents were generally used for the colour reactions, and the R_F values were calculated by the method of JERCHEL AND MÖHLE (E. Merck R_F-determination compasses).

Some fluorescent reactions were also detected by means of contact photography.

RESULTS

The colour reactions observed in visible and ultra-violet light are given in Table I. With the exception of *o*-cresol-phthaleincomplexone which was dissolved in a buffer solution of ammonium hydroxide–ammonium chloride (pH = 10.5), all reagents were dissolved only in distilled water or alcohol.

The sensitivity of each reaction under the above-mentioned conditions is given in Table II. The more sensitive reagents are found at the top of the table.

The selected solvent mixtures for the separation of yttrium from zirconium and their R_F values are given in Table III.

TABLE I

Reagent	*Solvent*	*Concn. % w/v*	*Yttrium*		*Zirconium*	
			Colour		*Colour*	
			Visible	*U.V.Light*	*Visible*	*U.V.Light*
1. Pyridine(2-azo-4)-resorcinol	alc.	0.1	Purple red	(—)	Purple red	(—)
2. 1(2-Pyridyl-azo)-2-naphthol	alc.	0.1	Red	(—)	Pink	(—)
3. Chromazurol S	water	0.1	Blue	(—)	Blue-violet	(—)
4. *o*-Cresolphthalein-complexone	buffer	0.1	Blue-violet	Yellow-gr. F	Pink	Green F
5. Pyrocatechol violet	water	0.1	Violet	(—)	Blue-violet	(—)
6. Na-rhodizonate HCl vapour	water	0.1	(—)	(—)	Yellow	Yellow F
7. Alizarin	alc.	0.1	Blue-violet	(—)	Red-violet	(—)
8. Alizarinsulfonic acid	water	0.1	Red-violet	(—)	Light red	(—)
9. Quinalizarin	alc.	0.1	Blue	(—)	Red-violet	(—)
10. Purpurin	alc.	0.1	Blue-violet	(—)	Red-violet	(—)
11. Chrysacine	alc.	0.1	Light red	Red F	Pink	Pink F
12. Murexide	water	0.1	Yellow	(—)	Yellow	Yellow F
13. 8-Hydroxyquinoline	alc.	0.5	Yellow	Yellow F	Yellow	Yellow F
14. *p*-Quinonetetrakis-diisopropylphosphonate	alc.	0.5	(—)	Yellow F	(—)	Yellow F
15. Quercetin	alc.	0.5	Yellow	Yellow-gr. F	Yellow	Yellow-gr. F
16. Morin	alc.	0.1	Yellow	Green F	Yellow	Green F
17. *α,α'*-Dipyridyl	alc.	0.5	(—)	Light blue F	(—)	Light blue F
18. *β*-Nitroso-*α*-naphthol	alc.	0.1	Orange	(—)	Light red	(—)
19. Aluminon	water	0.1	Red	(—)	Light red	(—)
20. Hematoxylin NH$_3$ vapour	alc.	0.1	Blue-violet	(—)	Red-violet	(—)
21. Diphenylcarbazone	alc.	0.1	Pink	(—)	Pink	(—)
22. Eriochrome Black T	water	0.1	Blue-violet	(—)	Red-violet	(—)

F = Fluorescence
gr = green

TABLE II

Reagent	*Yttrium*				*Zirconium*			
	1 µg	*5 µg*	*10 µg*	*15 µg*	*1 µg*	*5 µg*	*10 µg*	*15 µg*
1. Pyridine(2-azo-4)-resorcinol	+++				+++			
2. Pyrocatechol violet	+++				+++			
3. Chromazurol S	+++				+++			
4. Alizarin	++	+++			++	+++		
5. 8-Hydroxyquinoline	++	+++			++	+++		
6. Quercetin	++	+++			++	+++		
7. Hematoxylin, NH$_3$ vapour	++	+++			++	+++		
8. Diphenyl carbazone	++	+++			++	+++		
9. Purpurin	++	+++			++	+++		
10. Chrysacine	++	+++			++	+++		
11. Quinalizarin	++	++	+++		++	+++		
12. *β*-Nitroso-*α*-naphthol	+	++	+++		++	+++		
13. Morin	+	++	+++		++	+++		
14. Aluminon	+	++	+++		++	+++		
15. *p*-Quinonetetrakis-diisopropyl-phosphonate	++	+++			+	++	+++	
16. *α,α'*-Dipyridyl	+	++	+++		+	++	+++	

TABLE II (continued)

Reagent	Yttrium				Zirconium			
	1 μg	*5 μg*	*10 μg*	*15 μg*	*1 μg*	*5 μg*	*10 μg*	*15 μg*
17. Alizarinsulfonic acid	+	++	++	++	+	++	+++	
18. 1(2-Pyridyl-azo) 2-naphthol	++	+++			+	+	+	++
19. *o*-Cresolphthalein-complexone	+	+	++	++	++	+++		
20. Na-rhodizonate, HCl vapour	(—)	(—)	(—)	(—)	++	+++		
21. Murexide	+	+	++	+++	+	+	++	+++
22. Eriochrome Black-T	+	+	+	++	+	+	+	++

— = Negative; + = Positive; +++ = Strong positive

TABLE III

Solvents	Time	R_F values	
		Yttrium	*Zirconium*
1. Methanol : *n*-butanol : collidine : 6 *N*-acetic acid 2 : 1 : 1 : 1	4 h	0.76	no migration
2. Methanol : *n*-butanol : collidine : 6 *N*-acetic acid 1 : 1 : 2 : 1	5 h	0.66	no migration
3. Methanol : isopropanol : water : formic acid : ammonium formate 25 : 15 : 7.5 : 1 : 1	3 h	0.59	no migration
4. Formamide : ethanol : methanol : KSCN 10 : 10 : 10 : 0.2	1½ h	0.64	0.36
5. *n*-Propanol : water : hydrochloric acid : NH_4Cl 7 : 7 : 1 : 0.2	4 h	0.64	0.40
6. *n*-Propanol : water : hydrochloric acid : NH_4Cl 30 : 10 : 2 : 1	4 h	0.27	0.10

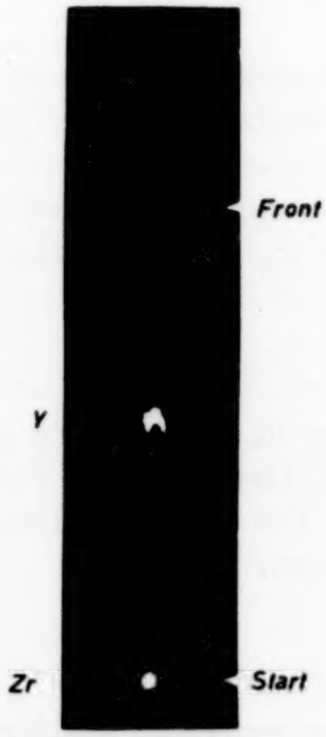

Fig. 1. Contact photography after chromatographic separation of yttrium from zirconium. Quantity 15 μg. Detecting reagent 8-hydroxyquinoline. Exposure time 20 sec. (Photographic paper Agfa-Brovira).

Fig. 1 shows a contact photograph of yttrium and zirconium after separation with a solvent mixture containing methyl alcohol, isopropyl alcohol, water, formic acid, and ammonium formate (12 : 8 : 4 : 0.6 : 0.2). The detecting reagent was 8-hydroxyquinoline. The two spots of the elements can be clearly distinguished.

DISCUSSION

Owing to the radiobiochemical importance of yttrium and zirconium as fission products or as daughter elements of strontium, our intention was to study complex formation between these two elements and different organic materials. A part of this study is reported in the present paper. For special reasons most reactions were carried out at room temperature and at a neutral pH (with the exception of *o*-cresolphthaleincomplexone); the fact that a change in the pH or an increase in the temperature could accelerate the formation of the complex was not taken into consideration. Some of the organic reagents used are well-known to form complexes with other elements, *i.e.* murexide with calcium[26-27], and *o*-cresolphthaleincomplexone[28-30], eriochrome black T[31] with barium, calcium, strontium, etc. Other reagents were selected as being likely to form complexes because of their chemical structure. Special attention was paid to alizarin derivatives. Some of the reagents were found to be very suitable for the determination of yttrium and zirconium because amounts as small as 1 μg could be detected. The colour reaction between *o*-cresol-phthaleincomplexone and yttrium or zirconium in visible and ultra-violet light was found to be more stable than that of the corresponding calcium-*o*-cresol-phthaleincomplexone derivative. The intensity of colours changed in the course of time. The colours may generally be altered by treating the paper strips with ammonia or hydrochloric acid vapour, but the fluorescence of zirconium was found to persist even after this treatment; in the case of sodium rhodizonate, the fluorescence of zirconium appeared only after exposure to hydrochloric acid vapours. The fluorescence of these two elements could also be detected by contact photography.

As solvent mixtures, two groups of solvents were selected:

I. Those in which only yttrium migrated, whereas zirconium remained at the starting point.
II. Those in which both elements migrated but with different R_F values.

The choice of solvent depends on the circumstances.

CONCLUSION

Some supplementary reactions for yttrium and zirconium are reported and their significance has been discussed. The amount which can detected varies from 1 to 30 μg according to the reagent. The colour reactions may be adapted for the determination of yttrium and zirconium.

ACKNOWLEDGEMENTS

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SUMMARY

The colour reactions of yttrium and zirconium with some organic reagents have been investigated and their sensitivity is reported. Some fluorescent reactions in ultra-violet light are also described and solvent mixtures for the separation of the two elements by paper chromatography are given.

RÉSUMÉ

Les auteurs ont examiné les réactions de coloration de l'yttrium et du zirconium obtenues avec des réactifs organiques, de même que des réactions de fluorescence en lumière ultraviolette. Ils ont effectué également une étude sur la séparation de ces deux éléments par chromatographie sur papier.

ZUSAMMENFASSUNG

Es wird über Untersuchungen von Farbreaktionen des Yttriums und des Zirkons mit einigen organischen Verbindungen im sichtbaren und U.V.-Gebiet berichtet, die papierchromatographische Nachweisempfindlichkeit dieser Reaktionen angegeben sowie die Lösungsmittel zur papierchromatographischen Trennung der beiden Elemente beschrieben.

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POLAROMETRISCHE BESTIMMUNG VON ZIRKONIUM(IV) MIT TARTRAZIN

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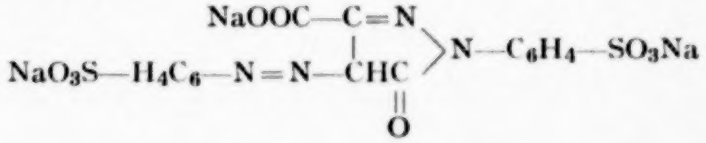
In der chemischen Fachliteratur kommt eine einzige Methode[1] zur polarometrischen Bestimmung von Zr(IV) vor, im welcher eine Cupferron-Standardlösung als Reagens herangezogen wurde.

Diese Methode wurde für Analysen von Proben mit Uranium–Niobium und Zirkoniumgehalt[2] zur Anwendung gebracht.

In der vorliegenden Arbeit wird die polarometrische Bestimmung von Zr(IV) und Zr(IV) bei Anwesenheit von U(VI) unter Anwendung von Tartrazin als Reagens für die Titrierung vorgeschlagen.



Tartrazin wurde zur gravimetrischen Bestimmung von Zirkonium[3] angewandt. Zirkonium bildet mit Tartrazin eine einheitliche Verbindung, deren Formel Zr_3 (Tartrazin) $(OOH)_3$ ist.

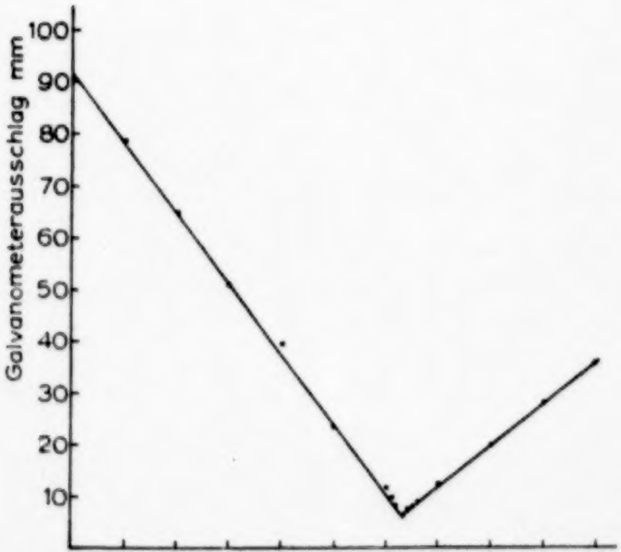


Fig. 1. Diagramm der Titration von 0.5 ml Zirkonilnitratlösung (0.006455 g Zr/ml) mit Tartrazin.

Die einheitliche Verbindung des Niederschlags hat uns dazu bewogen, für die polarometrische Titrierung von Zr(IV) Tartrazin zu benützen.

ARBEITSWEISE

Als Reagens wird eine 0.1%-ige Tartrazinlösung benützt.

Gearbeitet wird mit einer Lösung von salpetersaurem Zirkonilnitrat (RIEDL DE HÄEN) mit einem Gehalt von 0.006455 g Zr/ml.

Der Äquivalentspunkt wird an einem Polarograph-System HEYROVSKY, Type L.P. 55, Modell 1958 abgelesen. Wir arbeiten mit einer Einrichtung für polarometrische Titrationen mit einer gesonderten Bezugselektrode nach A. NEUBERGER.

Der Sauerstoff wird aus der Lösung mittels eines Wasserstoffstroms entfernt.

Am Anfang einer jeden Bestimmung wird Sauerstoff 10 Minuten lang und nach Zusatz jeder einzelnen Menge des Reagens je 30 Sekunden lang durchgeleitet.

Die Titrierung erfolgt bei einem Potential von —0.9 V.

Die Schwankung der Diffusionsstrom-Stärke während der Durchführung einer Bestimmung wird in Fig. 1 dargestellt.

Die Ergebnisse der polarometrischen Titrierung von Zr(IV) sind in der Tabelle I angeführt:

TABELLE I

Nr. der Bestimmung	*Zirkonilnitrat Lösung ml*	*Zirkoniumgehalt der Probe µg*	*Gefunden Zirkonium µg*	*Differenz %*
1	0.1	645.5	639.2	—1.01
2	0.15	968.2	957.1	—1.15
3	0.25	1613.7	1613.7	—
4	0.30	1936.5	1936.5	—
5	0.40	2682.–	2739.8	+2.15
6	0.50	3227.5	3227.5	—
7	0.50	3227.5	3201.9	—0.79
8	0.50	3227.5	3227.5	—
9	0.75	4841.3	4831.–	—0.21
10	1.00	6455.–	6501.1	+0.71

Die Fehlergrenze der Bestimmungen ist höchstens 2%.

In der Folge wurde eine Reihe von polarometrischen Bestimmungen durchgeführt von Zirkonium bei Anwesenheit von Uranium, deren Ergebnisse in der Tabelle II angeführt sind:

TABELLE II

Nr. der Bestimmung	*Zirkonilnitrat Lösung ml*	*Zirkoniumgehalt der Probe µg*	*Uranilnitrat Lösung ml*	*Uraniumgehalt der Probe µg*	*Gefunden Zirkonium µg*	*Differenz %*	*Verhältnis Zr:U*
1	0.25	1613.7	3	37.440	1603.3	—0.64	1:23
2	0.5	3227.5	3	37.440	3227.5	—	1:12
3	0.5	3227.5	3	37.440	3200.—	—0.85	1:12
4	0.5	3227.5	5	62.400	3227.5	—	1:19
5	0.5	3227.5	5	62.400	3227.5	—	1:19
6	0.5	3227.5	10	124.800	3227.5	—	1:39
7	0.5	3227.5	5	62.400	3176.3	—1.58	1:19
8	0.5	3227.5	5	62.400	3210.8	—0.52	1:19
9	0.6	3873.—	6	74.880	3806.2	—1.72	1:19
10	0.6	3873.—	6	74.880	3817.4	—1.43	1:19

Auf Grund der Untersuchung der Ergebnisse aus Tabelle II wird festgestellt, dass die von uns vorgeschlagene Methode eine polarometrische Bestimmung von Zr(IV) bei Anwesenheit von U(VI) bis Verhältnis 1:39 zulässt.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur polarometrischen Bestimmung von Zr(IV) unter Anwendung von Tartrazin als Reagens vorgeschlagen.

Die neue Methode ermöglicht eine Mikrobestimmung von Zirkonium, auch bei Anwesenheit von Uran bis zum Verhältnis 1:39, wobei die Fehlergrenze der Bestimmungen höchstens 2% ausmacht.

SUMMARY

A new polarimetric procedure has been developed for the rapid determination of zirconium in the presence of tartrazin as reagent. This determination is possible in the presence of uranium.

RÉSUMÉ

Les auteurs proposent une nouvelle méthode de dosage polarométrique du zirconium, au moyen de tartrazine comme réactif. Ce dosage peut s'effectuer en présence d'uranium.

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Bemerkung zu einer Arbeit von Kovács und Tárnoky

Jüngst erschien in dieser Zeitschrift eine Arbeit der im Titel genannten Autoren, die sich mit der komplexometrischen Titration von Calcium und Magnesium befasst. Hierbei wird Plasmocorinth B als Indicator verwendet. Es sei an dieser Stelle nicht darauf eingegangen inwieweit die Autoren korrekt sind, wenn sie sagen, dass das „rote Plasmocorinth B einen farbigen Komplex mit EDTA" bildet. Es sei hier lediglich bemerkt, dass die Autoren es nicht der Mühe wert fanden in Betracht zu ziehen, dass Firmennamen bei Farbstoffen gar nichts besagen und nur die chemische Konstitution Bedeutung hat, wenn man in der Literatur forscht. So ist es ihnen entgangen, dass derselbe Farbstoff auch unter dem Namen Eriochromblau SE von der Fa. Geigy in Basel hergestellt wird und unter diesem Namen vor einiger Zeit bereits als komplexometrischer Indicator verwendet wurde. Vom Schreiber dieser Zeilen und seinen Mitarbeitern wurde die Abkürzung Erio SE eingeführt. Die Verwendung von Erio SE wurde zuerst für die Calcium und Magnesiumbestimmung (in Serum) beschrieben[2] und später auch auf andere Metallionen ausgedehnt[3]. Beide Arbeiten sowie eine eingehende Literaturübersicht[4] sind an durchaus leicht zugänglichen Stellen publiziert worden.

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Short Communication

Paper electrophoresis of inorganic anions in sodium carbonate solution

The electromigration of ionorganic anions has been studied in few electrolytes. LEDERER AND WARD[1] used normal solutions of KCl, and more recently studies were reported in which ammonium carbonate[2,3] and 0.01 N NaOH[4] were used as electrolytes. While this manuscript was in preparation GRASSINI AND LEDERER[5] reported the use of 0.1 N NaOH in the paper electrophoresis of a number of inorganic anions.

LEDERER[2] reported the successful separation of a number of halogen oxyacids but found that periodate divided into two spots which moved little, and gave a reduction comet. He also reported difficulty due to liquid flow as a result of evaporation and lack of saturation of the paper.

It was thought that sodium carbonate might be a suitable electrolyte since it is fairly alkaline, has a suitable electrolytic strength, and is not volatile. Although this latter feature would preclude the use of indicators to detect the spots it would allow the electrophoresis apparatus to be operated at a higher voltage, thus enhancing the possibility of achieving satisfactory separations. To further minimize trouble due to evaporation the paper was sandwiched with a thin sheet of polyvinylchloride between two sheets of plate glass.

EXPERIMENTAL

The electrophoresis chamber and high-voltage potentiostat were designed and built in this Department.

The solutions were prepared from "Analytical Grade" reagents in distilled water and were decimolar unless otherwise indicated. A 2% solution of sodium carbonate in water was used as the electrolyte.

The electrolyte tanks were filled with a 2% aqueous solution of sodium carbonate to a constant mark about 2 cm below the glass plate, the levels being adjusted by means of a removable siphon filled by suction through a three way T-stopcock.

Whatman No. 3MM paper was used for the results reported. The starting line and starting positions were marked with a graphite pencil. The paper strip was drawn through the electrolyte and lightly blotted by placing between sheets of blotting paper and drawing a roller (weighing 1 kg) along the strip without applying additional pressure[6]. The paper was then placed at once on the lower glass plate, centered over a line drawn across the middle of this plate. A thin sheet of polyvinylchloride was placed between the paper strip and the upper glass plate. This sheet had five holes of 0.5 cm diameter drilled in a line across the centre, starting 1.5 cm from the edge and spaced 1.2 cm apart. Thirty minutes was allowed for capillary rise of the electrolyte from the tanks. After this time inflow is very small and starting the experimental runs in the centre virtually eliminates the effect of any unsaturation of the paper since any solution inflow subsides before the ions reach the regions of more rapid inflow. The upper glass plate was then removed and the test solutions applied through the holes in the polyvinylchloride sheet, the glass plate replaced and the potential applied at once. Test solutions were applied by means of a small platinum loop. The loop used, deposited a spot which spread to a diameter of about 3–4 mm soon after application.

A potential of 300 V was applied for one hour at currents of less than 39 mA.

After electrophoresis the papers were dried and then sprayed with the appropriate detecting reagent using an atomiser operated by compressed air.

To get comparable results from run to run, chromate was placed on all sheets to act as a marker ion. Movements of chromate ions varied slightly from sheet to sheet due apparently to small variations in the potential from the supply unit and perhaps impurities in the paper. Movements reported have been corrected to the equivalent of a chromate movement of 75 mm, this being an average value for all sheets run. Where more than one result has been obtained for any ion each result is shown separately.

TABLE I

Anion	Movement (mm)	Anion	Movement (mm)
Ferricyanide	76	Vanadate	50
Ferrocyanide	71	Nitrite	80
Chlorate	74	Sulphate	66
Bromate	61	Thiosulphate	84
Bromate ($M/40$)	59	Thiocyanate	76
Iodate	36	Chloride (M)	101
Iodate ($M/40$)	36	Bromide (M)	103
Periodate ($M/40$)	0	Iodide (M)	92
Molybdate	64		

CONCLUSIONS

From the results obtained with the 15 anions examined, it would appear that similar separations to those obtained with ammonium carbonate may be achieved using sodium carbonate. A separation of molybdate and vanadate was noted, which was not obtained by LEDERER with ammonium carbonate.

Reproducibility was good, being well within 5% in all cases.

Some difficulty was experienced in attempting to use test solutions of the same molarity for comparative purposes, being limited on one hand by the comparative insolubility of some anions, and by lack of sufficiently sensitive means of detection on the other. In most cases a 0.1 M solution was used, being sufficiently strong to permit satisfactory detection, and not so strong as to produce an undesirably large spot or tailing.

The halides were run as molar solutions as it proved impossible to detect 0.1 M solutions with certainty with available methods of detection. A molar solution of chromate was used to correct the movements in these instances.

Results obtained with periodate on Whatman 1, 2, 4 and 7 papers were similar to those previously reported[3,5]. With 2% sodium carbonate, 1% sodium carbonate – 1% sodium bicarbonate, and 2% ammonium carbonate solutions as electrolytes, and with an applied potential of 150 V, periodate gave reduction comets and travelled 25 mm, 31 mm, 25 mm respectively, relative to chromate 48 mm in each case. With Whatman 3 MM paper periodate gave a single spot which scarcely moved from the starting line, possibly because of adsorption by some impurity not present in the other papers.

The use of sodium carbonate as an electrolyte allows separations comparable to those previously reported but has the defect that acid–base indicator solutions cannot be used as universal indicators.

The authors wish to thank Mr. W. T. DENHOLM for designing the high-voltage potentiostat used in this study.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

V[1]. A SIMPLE METHOD OF CALCULATING ACID – BASE TITRATION ERRORS

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The calculation of titrimetric errors receives relatively infrequent attention in standard texts[2], an empirical treatment more often being given[3], while the accounts in the literature tend to be impracticably, sometimes unrealistically, complicated[4]. If sets of theoretical titration curves are prepared, errors can readily be assessed by inspection[5], but where such aids are not to hand, the errors can be calculated directly from the colour transition intervals of the indicators and the ionisation constants of the electrolytes concerned.

The titration error is made up of three parts:

(a) the *chemical error* due to the difference between the end-point (at which the indicator changes colour) and the equivalence point (the theoretical neutral point);

(b) the *visual discrimination error* which is a measure of the scatter caused by the limited ability of the eye exactly to remember or compare colours, and corresponds to an interval of about 0.1 pH unit; and

(c) the *indicator error* due to consumption of the titrant by the indicator itself.

Factors (b) and (c) are normally small compared with (a), which is the factor of principal interest in this paper.

Equivalence and end-point conditions

Before the assessment of errors, or indeed selection of the appropriate indicator, is possible, the hydrogen ion concentration or pH of the titration solution at these points must be known. The hydrogen ion concentration ζ (and pζ the pH) at the equivalence point is the calculated value for a solution of the pure salt in pure solvent, and in the case of strong acid – strong base titrations is equal to $K_w^{\frac{1}{2}}$. In other cases, ζ is the hydrogen ion concentration of the hydrolysed salt solution of appropriate concentration, and is calculated from the ionisation constant of the weak electrolyte in the usual way[5]. The end-point is the point at which the indicator changes colour, or, more strictly, the hydrogen ion concentration χ at which the indicator reaches the chosen colour. The value of χ may be determined from the pH of the comparison buffer solution, or from the known colour change interval of the indicator. When the chosen colour is the first perceptible colour change of the indicator, χ is given by the extreme value of the colour change interval. With an acid titrant, $p\chi$ is the upper extreme, and with an alkaline titrant the lower extreme of the indicator pH interval. For example, with methyl red the pH interval is 4.4 to 6.0; with an acid titrant $p\chi$ will be 6.0, with an alkaline titrant $p\chi$ will be 4.4. Where the actual interval is not known, but the indicator constant pK_{ind} is available, the end-points can be taken to be at $p\chi = pK_{ind} \pm 1$.

The sign, or sense, of the error

Even in the most rigorous and comprehensive treatment[4] it is not possible to define the sign, positive or negative, of the error mathematically, since it will depend on whether the acid or the base is the titrant. Definition of the sign by inspection, however, permits a simple treatment. The error itself is defined as,

$$\text{Relative error} = k\,\frac{\dfrac{\text{equivalence point}}{\text{volume of titrant}} - \dfrac{\text{end-point}}{\text{volume of titrant}}}{\text{equivalence point volume of titrant}} \quad \ldots\ldots\ldots \quad (1)$$

Conditions	*(k = sign of error)*	
	Acid titrant	*Base titrant*
$p\chi > p\zeta$	negative	positive
$p\chi < p\zeta$	positive	negative

The sign of the values given by the expressions below is a useful check on the values of χ and ζ used, since if the sign is negative before the application of k, this implies that impossible conditions are being applied to the titration. It will be observed in the expressions below that those derived for $p\chi > p\zeta$ contain the simple substitution of K_w/χ for χ in those derived for $p\chi < p\zeta$. Furthermore, unless the neutral salt concentration is excessive[4], activity coefficients may be neglected with very little error. The treatment is developed for monobasic acids and monoacid bases, and may be extended to polybasic or polyacidic compounds by substituting normalities for molarities.

THE CHEMICAL ERROR

1. *Strong acid – strong base titrations*

I. *$p\chi$ less than $p\zeta$.* If V ml of base of concentration M_B be titrated with an acid of concentration M_A, and the contribution of ions from the solvent is ignored (*vide infra*), then,

(i) the equivalence point volume of titrant

$$= V\,\frac{M_B}{M_A}\ \text{ml}$$

(ii) the total volume of the titration solution at this point will be

$$V + V\frac{M_B}{M_A} = V\left(\frac{M_A + M_B}{M_A}\right)\ \text{ml}$$

(iii) the numerator of expression (1) will be given by, as a first approximation ignoring solvent ionisation, the volume of titrant required to produce a hydrogen ion concentration of χ in the equivalence point volume of solution, *viz.*,

$$\frac{\chi\,V(M_A + M_B)}{{M_A}^2}$$

(iv) the relative error is then, from (1),

$$\frac{\chi\, V\,(M_A + M_B)}{M_A^2} \times \frac{1}{V\,\frac{M_B}{M_A}}$$

(v) the percentage error $E\%$ is then 100 times this,

$$E\% = \frac{100\,(M_A + M_B)\,\chi}{M_A M_B} \quad \dots\dots\dots\dots\dots \quad (2)$$

If the two solutions are equivalent, and $M_A = M_B = M$,

$$E\% = \frac{200\,\chi}{M} \quad \dots\dots\dots\dots\dots \quad (2a)$$

If the base is the titrant, χ will, for the same indicator, have a different value from that used for the acid titrant, but the resultant expression for $E\%$ is identical with (2), and is derived by calculating the amount of acid unneutralised at the end-point in step (iii).

II. pχ *greater than* pζ. The expression is derived through the same argument as before. Working in terms of hydroxyl ion, the steps are parallel to those above. Working in terms of hydrogen ion, the amount of acid of equivalent concentration required to neutralise the amount of hydroxyl ion left at the end-point may be calculated. By either method, the following expression results

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\,\frac{K_w}{\chi} \quad \dots\dots\dots\dots\dots \quad (3)$$

These expressions are adequate when pχ is less than 6 or greater than 8, but as pχ approaches pζ, or $\frac{1}{2}$pK_w, the contribution of ions from the solvent becomes more significant.

Ionisation of the solvent. When pχ is close to $\frac{1}{2}$pK_w, the amount of hydrogen or hydroxyl ions contributed by the solvent has to be subtracted from the amount to be supplied by the titrant in step (iii) above. When p$\chi <$ pζ the solvent contribution of hydrogen ions, from the ion product of water, will be equal to the total hydroxyl ion concentration at the end-point, *i.e.*, K_w/χ, and expression (2) becomes in the exact form

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\chi - \frac{K_w}{\chi}\right) \quad \dots\dots\dots\dots\dots \quad (4)$$

By a similar argument, when p$\chi >$ pζ, expression (3) becomes in the exact form

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \chi\right) \quad \dots\dots\dots\dots\dots \quad (5)$$

2. *Weak acid – strong base titrations*

In the presence of *excess of strong base* pχ will be greater than pζ and expression (3) applies.

In the presence of *excess of weak acid* pχ will be less than pζ and the solution will contain an acid buffer. Ignoring hydrolysis, the hydrogen ion concentration of the solution is given by the buffer equation[5],

$$[\mathrm{H}^+] = \frac{c_a}{c_s}\,K_a \quad \dots\dots\dots\dots\dots \quad (6)$$

where c_a and c_s are the weak acid and salt concentrations, and K_a is the ionisation constant of the weak acid. If V ml of strong base of concentration M_B is titrated with a weak acid of concentration M_A, ignoring hydrolysis and ionisation of solvent (*vide infra*) then,

(i) the volume of acid titrant required to reach the equivalence point

$$= V\frac{M_B}{M_A} \text{ ml}$$

(ii) the total volume of the titration solution at this point will be

$$V + V\frac{M_B}{M_A} = V\left(\frac{M_A + M_B}{M_A}\right) \text{ ml}$$

(iii) the salt concentration will be

$$c_s = \frac{M_B V}{V\left(\dfrac{M_A + M_B}{M_A}\right)} = \frac{M_A M_B}{(M_A + M_B)}$$

(iv) from (6) the concentration of free weak acid in conjunction with this salt concentration to give a solution of pH = pχ at the end-point will be

$$c_a = \frac{M_A M_B}{M_A + M_B} \cdot \frac{\chi}{K_a}$$

(v) the volume of acid titrant of concentration M_A required to give this concentration in the volume of solution defined in step (ii) will be

$$\text{volume} = \frac{M_A M_B}{M_A + M_B} \cdot \frac{\chi}{K_a} \cdot \frac{V(M_A + M_B)}{M_A^2} = \frac{M_B V \chi}{M_A K_a} \text{ ml}$$

This is then the numerator in (1).

(vi) The relative error from (1) is then

$$\frac{M_B V \chi}{M_A K_a} \cdot \frac{M_A}{M_B V} = \frac{\chi}{K_a}$$

(vii) the percentage error $E\%$ is then 100 times this,

$$E\% = \frac{100\,\chi}{K_a} \qquad (7)$$

This very simple expression is independent of titrant and titrand concentration, and is applicable to acids with ionisation constants as low as 10^{-7} at concentrations around decimolar without loss of accuracy. With the strong base as titrant and the appropriate value of χ the same expression results, but the sign, k, will now be negative.

3. *Strong acid – weak base titrations*

As before, in the presence of *excess of strong acid*, expression (2) is valid. In the presence of *excess of weak base*, an argument similar to that above yields the expression for the percentage error $E\%$

$$E\% = \frac{100\,K_w}{\chi\,K_b} \qquad (8)$$

This expression is also concentration independent, and is applicable to bases of ionisation constant as low as 10^{-7}.

Beyond the limits stated, it will be found that expressions (7) and (8) predict errors greater than those found in practice. Expressions (2) and (3) will similarly be found defective when applied to weak acid or base titrations. In such cases, the hydrolysis of the salt has to be taken into account. In a rigorous treatment, allowance must also be made for ionisation of the solvent, although in practice this factor makes a very small contribution, as can be shown by solution of expressions (27) to (30) for numerical examples, and can normally be neglected.

Hydrolysis of salts. It is necessary to distinguish between excess of strong electrolyte and excess of weak electrolyte. In both circumstances hydrolysis produces hydrogen or hydroxyl ions, depending on the nature of the salt, which contribute to the numerator of expression (1) and so reduce the amount of such ions which has to be furnished or neutralised by the titrant to reach the end point. At the same time, the value of c_s is reduced by the amount of salt lost by hydrolysis; this is a secondary effect which will be considered later. Two cases of each circumstance require consideration, and the sign of the error, k, being dependent on the nature of the titrant, is determined by inspection as described above.

Excess of strong acid in the titration of a weak base

The hydrogen ion concentration of the solution of the hydrolysed salt in the presence of an excess of strong acid of concentration calculated to be c_A is given by[5]

$$[\mathrm{H}^+] = {}^1/_2 \left\{ \left(c_A{}^2 + \frac{4K_w c_s}{K_b} \right)^{\frac{1}{2}} + c_A \right\} \quad \ldots \ldots \quad (9)$$

which must derive from

$$[\mathrm{H}^+]^2 - c_A[\mathrm{H}^+] - \frac{K_w c_s}{K_b} = 0 \quad \ldots \ldots \quad (10)$$

whence,

$$c_A = \left([\mathrm{H}^+] - \frac{K_w c_s}{[\mathrm{H}^+] K_b} \right) \quad \ldots \ldots \quad (11)$$

At the end-point, $[\mathrm{H}^+] = \chi$, and c_A corresponds to the excess of acid required to produce the chosen end-point colour, and by arguments similar to those given in the derivation of (2) the percentage error $E\%$ will be,

$$E\% = \frac{100(M_A + M_B)\, c_A}{M_A M_B} \quad \ldots \ldots \quad (12)$$

Substitution of (11) in (12) then gives the error corrected for hydrolysis,

$$E\% = \frac{100(M_A + M_B)}{M_A M_B} \left(\chi - \frac{K_w c_s}{\chi\, K_b} \right) \quad \ldots \ldots \quad (13)$$

If required, the value of c_s (from step (iii), equation 7) can be inserted in this expression, giving

$$E\% = 100 \left\{ \frac{(M_A + M_B)\,\chi}{M_A M_B} - \frac{K_w}{\chi\, K_b} \right\} \quad \ldots \ldots \quad (13a)$$

Excess of strong base in the titration of a weak acid

If the excess of strong base is calculated to be c_B, the hydroxyl concentration is given by[5]

$$[\mathrm{OH^-}] = {}^1/_2 \left\{\left(c_B{}^2 + \frac{4K_w c_s}{K_a}\right)^{\frac{1}{2}} + c_B\right\} \quad \ldots\ldots\ldots\ldots \quad (14)$$

whence, as before,

$$c_B = \frac{K_w}{[\mathrm{H^+}]} - \frac{[\mathrm{H^+}]c_s}{K_a} \quad \ldots\ldots\ldots\ldots \quad (15)$$

and, as above,

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \frac{\chi\, c_s}{K_a}\right) \quad \ldots\ldots\ldots\ldots \quad (16)$$

Excess of weak acid in the titration of a strong base

The hydrogen ion concentration for a calculated excess of acid c_a is given by[5]

$$c_s[\mathrm{H^+}]^2 - (K_w + c_a K_a)[\mathrm{H^+}] - K_w K_a = 0 \quad \ldots\ldots\ldots\ldots \quad (17)$$

whence

$$c_a = \frac{c_s[\mathrm{H^+}]^2 - K_w([\mathrm{H^+}] + K_a)}{K_a[\mathrm{H^+}]} \quad \ldots\ldots\ldots\ldots \quad (18)$$

At the end-point, $[\mathrm{H^+}] = \chi$, and c_a is the concentration required in step (iv) in the derivation of (7), and by a similar argument, the percentage error $E\%$ will be

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{c_s\chi^2 - K_w(\chi + K_a)}{K_a\,\chi}\right) \quad \ldots\ldots\ldots\ldots \quad (19)$$

Excess of weak base in the titration of a strong acid

The hydrogen ion concentration for a calculated excess of weak base c_b is given by[5]

$$K_b[\mathrm{H^+}]^2 + (K_w + K_b c_b)[\mathrm{H^+}] - c_s K_w = 0 \quad \ldots\ldots\ldots\ldots \quad (20)$$

whence

$$c_b = \frac{K_w}{K_b}\left(\frac{c_s}{[\mathrm{H^+}]} - 1\right) - [\mathrm{H^+}] \quad \ldots\ldots\ldots\ldots \quad (21)$$

This gives a percentage error $E\%$ of

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left\{\frac{K_w}{K_b}\left(\frac{c_s}{\chi} - 1\right) - \chi\right\} \quad \ldots\ldots\ldots\ldots \quad (22)$$

Further corrections for decrease of salt concentration by hydrolysis and for ionisation of solvent

The expressions derived above suffice for most practical purposes, but rigorous treatment calls for two further adjustments. *Hydrolysis* of the salt causes a diminution in c_s. This is already included in equations (17) and (20), and therefore in (19) and (22), but where the strong acid or base is in excess, and hydrolysis is considerable, further adjustment of (13) and (16) is required. In the case of the *strong acid*, the cation of the weak base is hydrolysed,

$$B^+ + H_2O \rightleftarrows BOH + H^+$$

and the true concentration of B^+, assumed to be equal to c_s in the derivation of (9) is

$$[B^+] = c_s - [BOH]$$

From the ionisation constant of the base BOH and the ion product of water,

$$[B^+] = \frac{c_s[H^+]K_b}{[H^+]K_b + K_w} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (23)$$

Substitution of (23) for c_s in (13) then gives the percentage error corrected for loss of cation by hydrolysis

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\chi - \frac{K_w c_s}{\chi K_b + K_w}\right) \quad \ldots\ldots\ldots\ldots \quad (24)$$

In the case of the *strong base*, by a similar argument, the true value of $[A^-]$ is

$$[A^-] = \frac{c_s K_a}{K_a + [H^+]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (25)$$

and substitution of (25) for c_s in (16) gives the percentage error corrected for loss of anion by hydrolysis

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \frac{\chi c_s}{K_a + \chi}\right) \quad \ldots\ldots\ldots\ldots \quad (26)$$

Further refinement may be achieved by correcting for *ionisation of the solvent* in the same way as in (4) and (5). This finally yields expressions which are fully rigorous and exact under all conditions. In the four cases cited, the expressions including ionisation of the solvent become:

Excess of strong acid in the titration of a weak base:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\chi - \frac{c_s K_w}{\chi K_b + K_w} - \frac{K_w}{\chi}\right) \quad \ldots\ldots\ldots\ldots \quad (27)$$

Excess of strong base in the titration of a weak acid:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{K_w}{\chi} - \frac{\chi c_s}{K_a + \chi} - \chi\right) \quad \ldots\ldots\ldots\ldots \quad (28)$$

Excess of weak base in the titration of a strong acid:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left(\frac{c_s\chi^2 - K_w(\chi + K_a)}{K_a\chi} - \chi\right) \quad \ldots\ldots\ldots\ldots \quad (29)$$

Excess of weak acid in the titration of a strong base:

$$E\% = \frac{100\,(M_A + M_B)}{M_A M_B}\left\{\frac{K_w}{K_b}\left(\frac{c_s}{\chi} - 1\right) - \chi - \frac{K_w}{\chi}\right\} \quad \ldots\ldots\ldots\ldots \quad (30)$$

These further corrections make little difference to the value of the error, as solution for numerical examples would show, and are usually of less significance than the visual discrimination error.

THE VISUAL (OR INSTRUMENTAL) DISCRIMINATION ERROR

If the uncertainty in remembering or comparing colours corresponds to a pH interval of $\pm \Delta$ pH unit, then the end-point observed will fall within the pH range p$\chi \pm \Delta$, so that the hydrogen ion concentration at the end-point will be $\chi \cdot 10^{\mp\Delta}$. Consequently, in the expressions derived above, the percentage error, taking scatter into account will be

$$E \cdot 10^{\mp\Delta} \quad \ldots\ldots\ldots\ldots\ldots \quad (31)$$

With visual observation of the colour change, Δ is usually about 0.1 pH unit, or somewhat less. Consequently the refinements in the calculation of E in equations (23) to (30) are usually of little significance. However, when the end-point is detected photoelectrically or electrometrically, the instrumental discrimination error may be much less, and Δ may be as little as 0.01 pH unit, in which case the refinements of equations (23) to (30) may become significant.

THE INDICATOR ERROR

The amount of titrant consumed by the indicator is normally very small unless the titrant concentration is very low. It must be remembered that only a fraction, about one tenth, of the indicator is titrated to give a first perceptible colour change. This may, however, be misleading, since it will depend on the form in which the indicator is added to the titration solution. Thus, if the alkaline form of the indicator is added to the titrand, and the titrant is acid, approximately one tenth of the indicator is titrated, and the error is positive, but if the acid form of the indicator were used in this titration it would all react with the base, and only one tenth would be restored to the acid form at the end-point, so that the error would be negative and correspond to about nine tenths of the amount of the indicator added. If the indicator solution were adjusted to the first perceptible colour change in the correct direction, or otherwise conditioned to the chosen end-point colour before addition to the titration solution, the indicator error would theoretically be nil, and in practice negligible.

If the indicator is used in the *same form as the titrand*, then the amount of the titrant required to react with the indicator will be the volume of the indicator solution used, multiplied by its concentration, divided by the concentration of the titrant, and the whole multiplied by the fraction of the indicator changed, normally about one tenth:

$$\text{Titrant consumption} = \frac{v_{\text{ind}}\, c_{\text{ind}}}{M_{\text{titrant}}} \cdot \frac{1}{10}.$$

If the initial volume of the titrand is V ml, then the percentage error $E_I\%$ will be:

$$E_I\% = \frac{v_{\text{ind}}\, c_{\text{ind}}\, 100}{M_{\text{titrant}}\, V \dfrac{M_{\text{titrand}}}{M_{\text{titrant}}}} \cdot \frac{1}{10} = \frac{10\, v_{\text{ind}}\, c_{\text{ind}}}{V\, M_{\text{titrand}}} \quad \ldots\ldots\ldots \quad (32)$$

Most indicators are used in solutions of concentrations between 1.5 and $2.5 \cdot 10^{-3}\, M$, and the amount required in a titration is normally specified as n drops per 10 ml of titrand. If c_{ind} is taken as $2 \cdot 10^{-3}$ and the drop size as 0.05 ml, then

$$E_I\% = \frac{n \cdot 10^{-4}}{M_{\text{titrand}}} \quad \ldots\ldots\ldots\ldots\ldots \quad (33)$$

If the indicator is used in the *same form as the titrant*, then the percentage error becomes negative,

$$E_{\mathrm{I}}\% = -\frac{9\,n \cdot 10^{-4}}{M_{\mathrm{titrand}}} \quad \ldots\ldots\ldots\ldots \quad (34)$$

The total titration error is therefore,

$$\text{Total \% error} = E \cdot 10^{\mp 4} + E_{\mathrm{I}} \quad \ldots\ldots\ldots\ldots \quad (35)$$

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SUMMARY

The error in acid–base titrations is analysed into a chemical error due to disparity between end- and equivalence points, a visual (or instrumental) discrimination error due to uncertainty in remembering or comparing colours, and an indicator error due to consumption of titrant by the indicator. Simple expressions are derived for the calculation of the chemical error, and these are progressively refined ultimately to expressions which are rigorous and exact under all conditions.

RÉSUMÉ

L'erreur dans les titrages acide–base est analysée en trois composantes: l'erreur chimique, due à la différence existant entre le point final et le point équivalent; l'erreur visuelle due à l'incertitude de l'observateur lorsque celui-ci compare les couleurs; l'erreur d'indicateur due à la consommation de liqueur titrée par l'indicateur.

ZUSAMMENFASSUNG

Der Fehler bei Säuren–Basen Titrationen wird auf 3 Ursachen zurückgeführt: Nichtgleichheit des Endpunktes und Aequivalenzpunktes; Unsicherheit bei der Festlegung der Indikator-Farbnuance am Umschlagspunkt; Vernachlässigung des Verbrauchs an Titrierlösung durch den Indikator.

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THE SEPARATION AND DETERMINATION OF ALUMINUM IN PLUTONIUM-ALUMINUM ALLOYS*

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INTRODUCTION

Two methods have been reported for the determination of aluminum in plutonium–aluminum alloys. In one, developed by SMITH[1], plutonium is separated from aluminum by precipitation as the iodate. A mercury cathode is used to remove other interfering ions and aluminum is determined colorimetrically using aluminon. Although this procedure had not been applied to alloys of as high an aluminum content as were of interest in the work here, it did not appear likely that the precision could be improved sufficiently to meet the necessary requirements.

A second method, developed by CLEVELAND AND NANCE[2], measured the absorbance of the aluminum complex formed with oxine (8-quinolinol) in chloroform after plutonium is removed by precipitation and extraction as plutonium cupferrate.

Since both of these methods require operations difficult to carry out routinely with high precision in the glove box facilities in which plutonium is ordinarily handled, a simpler procedure was sought. The present work shows that an ion-exchange technique can be used to obtain a quantitative separation of aluminum and plutonium.

Colorimetric oxine and aluminon methods, a gravimetric oxine method, and volumetric oxine and EDTA methods were investigated for determining the aluminum after its separation from plutonium. Both the gravimetric and volumetric methods gave more precise results than either of the colorimetric methods. The precision and accuracy of the gravimetric and the volumetric methods are comparable, but the volumetric methods are faster.

PRINCIPLES OF THE ION-EXCHANGE SEPARATION

In a hydrochloric acid solution the ion-exchange behavior of both aluminum and plutonium(IV) is ideal for their separation. Plutonium(IV) forms anionic chloride complexes which are retained by an anion resin[3]. The higher the hydrochloric acid concentration, the greater the adsorption[4]. Table I, adapted in part from a graph by WISH[5], indicates this behavior.

Data on the distribution coefficients for iron(III) in hydrochloric acid are included in Table I to show how its behavior parallels that of plutonium(IV)[6]. Any interference from iron in the aluminum determination is obviated since the iron is retained on the column.

Aluminum does not form an anionic chloride complex at any hydrochloric acid

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TABLE I

INFLUENCE OF HCl CONCENTRATION ON ADSORPTION OF Pu(IV) AND Fe(III)

Pu: Dowex-2, Fe: Dowex-1

HCl N	*Distribution coefficient*	
	Pu(IV)	*Fe(III)*
1	0.10	0.33
2	0.15	1.94
4	0.40	67
6	30	460
8	1400	—
9	—	5900
10	5000	—
12	8000	—

concentration[7]. Plutonium and aluminum can be separated, therefore, by passing a solution of the two elements in 8 *N* or higher hydrochloric acid through an anion-exchange resin column. The plutonium is retained on the resin and the aluminum passes through. The plutonium can be eluted from the column with hydrochloric acid, 1 *N* or less in concentration.

REAGENTS

Al standard: (5.0 mg per ml). (Dissolve 5.000 g pure Al metal in HCl, dilute to 1 l). Dimethylglyoxime (1%): (Dissolve 1 g dimethylglyoxime in 100 ml 1% NaOH solution). Dowex® 1 × 4: (50–100 mesh, chloride form). Acid buffer: (108.9 g CH_3COONa and 2.3 ml glacial CH_3COOH diluted to 1 l). Basic buffer (26.5 g NH_4Cl and 7.5 ml conc. NH_4OH diluted to 1 l). EDTA: (ethylenedinitrilo) tetraacetic acid, 0.1 *M*. (Dry the disodium salt overnight at 80°, dissolve 37.22 g and dilute to exactly 1 l. Store in Pyrex or polyethylene bottle). $(CH_3COO)_2Zn$ (0.02 *M*) (Add two to three drops 8 *N* HCl per liter to prevent hydrolysis. Standardize against 0.1 *M* EDTA, using xylenol orange as indicator). Xylenol Orange (0.2%): (Dissolve 0.2 g in 100 ml H_2O). All other reagents used are of reagent grade.

PREPARATION AND TREATMENT OF THE ION-EXCHANGE COLUMN

An ion-exchange column was prepared by fitting a glass tube, 22 mm inside diameter and 35 cm long, with a stopcock and flaring the top. A small pad of glass wool was placed in the bottom of the column and it was filled to a height of 25 cm with resin that had been pretreated by washing several times with 8 *N* HCl. After filling, another small pad of glass wool was placed on top of the column and it was washed with approximately 250 ml of 8 *N* HCl. A column prepared in this manner will hold about 4 g of plutonium before regeneration is necessary. It can be regenerated using 0.4 to 1 *N* HCl.

Gas bubbles form within the column if plutonium is allowed to remain on the resin overnight. To prevent this, plutonium is eluted from the column at the end of each working day. If gas does form, it can be removed by stirring the column with a long glass rod.

METHOD

The size of an alloy sample to be used depends on its aluminum content. In developing the procedure which follows, 5 mg aluminum spikes were used. This could be varied, but appropriate changes would have to be made in column size and reagent concentrations.

Two ml of 8 *N* HCl are pipetted into a 10-dram vial. The alloy sample is added and allowed to dissolve completely. Then two ml of conc. HNO_3 are added slowly to oxidize the plutonium. This reaction generates heat and gas, so care must be exercised to prevent the solution from overflowing the vial. Oxidation is rapid: complete oxidation is indicated by a cessation of bubbling and a clear solution, deep brown when viewed under daylight-type fluorescent lights. After oxidation is complete, the solution is transferred to the resin column and eluted at 2 ml per min with 8 *N* HCl. Sixty ml of eluate are collected.

The aluminum is determined in the eluate by one of the following methods.

Gravimetric oxine method

The eluate is neutralized to the blue of the bromphenol blue end-point by the careful addition of conc. NH_4OH. Dilute HCl is added until the color of the solution just turns back to yellow. The aluminum is then precipitated with oxine using a procedure essentially the same as described in KOLTHOFF AND SANDELL[8]. It differs in that the oxine is prepared in 8 *N* HCl instead of CH_3COOH and the solution containing the precipitate is heated almost to boiling to coagulate the precipitate and then filtered instead of letting it stand for an hour before filtering.

Volumetric oxine method

The procedure used for the volumetric method is similar to the procedure described in KOLTHOFF AND SANDELL[9]. No indicator is used, however, for determining when sufficient $KBrO_3$ has been added to produce the necessary small excess of bromine. A number of indicators have been suggested[10], but none is recommended as being particularly effective. Experimenting with several confirmed this recommendation. Instead, in initial work a spot test was used. This involved withdrawing, periodically, a small quantity of sample solution on the end of a stirring rod and mixing it on a test plate with a solution containing KI and starch. When this KI-starch solution turned blue, an excess of bromine was present indicating that sufficient $KBrO_3$ had been added.

This same test can be used, if necessary, when production samples are being analyzed. But when the alloy composition is constant for a number of samples, all samples can be cut the same size, the volume of $KBrO_3$ necessary to provide a slight excess of bromine determined on the first sample and that volume used on all of the remaining samples.

Volumetric EDTA method

A back titration procedure is used. After adding 5.00 ml of 0.1 *M* EDTA and two drops of 0.1% bromcresol green indicator to the column eluate, neutralize the solution by the careful addition of 12 *N* NaOH. Then add 5 ml of the acid buffer solution, five drops of xylenol orange indicator and titrate to the purple end-point using 0.02 *M* $(CH_3COO)_2Zn$.

A blank is run on the plutonium used in the preparation of the synthetic alloy samples to correct for its Al content. In the synthetic alloy samples, the Al concentration is calculated using the following equation:

$$\text{mg Al} = 26.98\ (\text{mequivs. Zn for blank} - \text{mequivs. Zn for sample})$$

In a true alloy sample, the mequivs. Zn for the blank in the equation would be replaced by the mequivs. Zn equivalent to the amount of EDTA initially added.

It has been reported that in order to complete the reaction between Al and EDTA, it is necessary to boil the solution after the addition of the EDTA and the pH adjustment[11]. In this work it was found that if the EDTA is added before neutralization, the heat of neutralization is sufficient to ensure complete complexation of all the Al. Low results are obtained, however, if the solution is neutralized and allowed to cool before addition of the EDTA.

RESULTS AND DISCUSSION

Several methods are available for determining small amounts of aluminum. Five were selected for investigation: colorimetric oxine, colorimetric aluminon, gravimetric oxine, volumetric oxine and volumetric EDTA. The purpose of these investigations was to determine which of the methods was the most applicable to the samples and the working conditions. The methods were evaluated by analysis of a series of standard aluminum solutions.

The conclusion from this investigation was that the gravimetric oxine method and the two volumetric methods gave the best results. Not only was their precision better than either of the colorimetric methods, but also from an equipment and manipulation standpoint, the gravimetric and the volumetric methods offered less difficulty than did the colorimetric methods. This is a very important consideration when analytical work must be done in glove boxes.

Interferences

Interference would be expected from any cation that is not retained on the ion-exchange column and normally interferes with the method used for determining aluminum. In order to be retained on the resin column, the cation must form an anionic chloride complex in 8 *N* HCl. KRAUS AND NELSON[7] have summarized the anion-exchange behavior of a number of metal ions in hydrochloric acid solutions. From this summary, and from the knowledge of those metals that are usually found as impurities in samples, it was possible to anticipate interferences and alter methods to eliminate them.

Only iron, copper, nickel, chromium and aluminum have been present in samples at any one time in concentrations greater than 200 p.p.m. Of these, only iron is present consistently in high concentrations. Fortunately, iron(III) forms an anionic chloride complex which is retained by the resin. Chromium(III) is not retained by the resin. Its interference can be prevented, however, by oxidizing it to chromate[12,13].

The distribution coefficient for copper is quite low, so there was the possibility that it would come through the column[7]. If it did, it would interfere with all of the methods used for determining aluminum.

Nickel is not retained on the column and likewise will interfere with all of the methods used for determining aluminum.

A series of synthetic alloy samples were run to determine if copper was retained on the column and to determine the extent of interference from nickel. The results of these runs are shown in Table II. They indicate no interference from copper, but interference from nickel, if present in concentrations greater than 600 p.p.m. From these results it was apparent that the methods for determining aluminum had to be modified so that they could be used on those samples containing more than 600 p.p.m. nickel.

The literature offered several suggestions for determining aluminum in the presence of nickel. For the most part, however, they required either abandonment of the oxine or EDTA procedures or the use of equipment, such as a mercury cathode, that would

TABLE II

EFFECT OF Cu AND Ni ON Al DETERMINATION

Impurity	*Impurity concentration*		*Method of determination*	*% recovery Al*
	mg	*Equivs. p.p.m.*		
Cu	1.0	2000	oxine (vol)	100
Ni	1.0	2000	oxine (vol)	110
Ni	1.0	2000	EDTA	109
Ni	0.7	1400	EDTA	107
Ni	0.5	1000	oxine (vol)	105
Ni	0.5	1000	EDTA	105
Ni	0.4	800	EDTA	103
Ni	0.3	600	EDTA	100
Ni	0.2	400	EDTA	100
Ni	0.1	200	EDTA	100

be difficult to manipulate in a glove box. The one suggestion that did appear feasible was the removal of nickel by masking or precipitation.

Cyanide is the logical ion for masking nickel. It does not prevent the precipitation of aluminum with oxine[12] or the formation of the aluminum–EDTA complex[14]. However, cyanide would present difficulties with waste disposal, so other complexing agents as well as precipitating agents were investigated. These included the citrate, oxalate and sulfosalicylate ions, sodium sulfide and dimethylglyoxime. Of these, the only one that was satisfactory was dimethylglyoxime.

In the three methods that have been described for determining aluminum, the determination is carried out in a slightly acidic solution. This prevented the formation of aluminum hydroxide. But it was determined experimentally that nickel could not be completely precipitated by dimethylglyoxime from the sample solutions at a pH lower than 8. It was therefore necessary to modify the methods for determining aluminum.

In a basic solution, aluminum hydroxide formation can be prevented by the presence of the tartrate ion. Tartrate does not prevent the precipitation of aluminum with oxine or nickel with dimethylglyoxime. The volumetric oxine method was modified on the basis of this information. This modification involved the addition of 0.2 g sodium tartrate to the column eluant, then neutralization to the phenolphthalein end-point. Thirty ml of the basic buffer was added followed by 2 ml of the dimethylglyoxime solution. After waiting a few minutes to permit formation of the dimethylglyoximate, 3 ml of the oxine solution was added and the determination completed as in the original volumetric method.

Since nickel dimethylglyoximate is present in the aluminum oxinate precipitate, the determination cannot be completed gravimetrically. The dimethylglyoxime does not interfere in the volumetric method, however.

The EDTA method was modified to eliminate the interference from nickel in a manner comparable to that used in the volumetric oxine method. After collecting the eluant from the column, 0.2 g sodium tartrate was added and the solution neutralized to the phenolphthalein end-point by the careful addition of 12 *N* NaOH. Two ml of the dimethylglyoxime solution was added and the solution stirred for one minute. After standing for a minute, the solution was filtered through a medium porosity sintered glass filter funnel and the precipitate washed with 1% NaOH. Fifteen ml

8 *N* HCl was added to the combined filtrate and washings, then 5.00 ml 0.1 *M* EDTA. The determination was then completed following the original method.

Plutonium(IV) forms a precipitate with oxine[15] and a complex with EDTA[16]. To determine if there was enough plutonium leaking through the column to interfere in the aluminum determinations, a column was loaded with plutonium almost to capacity and a sample of the eluate then analyzed for plutonium. The eluate contained less than a mg of plutonium per l. This is too low to affect any of the methods given for determining aluminum.

TABLE III

PRECISION AND ACCURACY OF METHODS (SYNTHETIC ALLOYS)

Method	*No. samples*	*Al concn.*		*S.D.*
		Known	*Exp. mean*	
Oxine (grav.)	12	5.00 mg	5.03 mg	±0.11 mg
Oxine (vol.)	17	5.00 mg	4.93 mg	±0.08 mg
EDTA	12	5.00 mg	4.92 mg	±0.10 mg

Precision and accuracy of methods

The precision and accuracy of the oxine and EDTA methods for determining aluminum in an alloy were determined by running a series of synthetic alloy samples. These were prepared by dissolving 500-mg portions of pure plutonium metal and adding aliquots of the standard aluminum solution. The results are shown in Table III.

TABLE IV

PRECISION AND ACCURACY OF VOLUMETRIC METHODS (MODIFIED PROCEDURES)

Method	*Ni concn.*	*No. samples*	*Al concn.*		*S.D.*
			Known	*Exp. mean*	
Oxine	1 mg	11	5.00 mg	4.98 mg	±0.09 mg
EDTA	1 mg	6	5.00 mg	4.98 mg	±0.03 mg

A statistical analysis of duplicate results on 22 individual alloy samples run over a period of five weeks by the volumetric oxine method showed a standard deviation of ±0.012%. The nominal aluminum content of these alloys was 1%.

The precision and accuracy of the volumetric methods were determined using

TABLE V

COMPARISON OF PRECISION OF METHODS FOR DETERMINING ALUMINUM IN PLUTONIUM–ALUMINUM ALLOYS

Method	*Coefficient of variation*	*Comments*
Iodate-Aluminon	6.4%	Based on 28 determinations on synthetic samples in 0.2 to 0.4 w/o Al range.
Cupferron-Oxine (Colorimetric)	2.6%	Based on 24 determinations on synthetic 1 w/o Al alloy samples.
Ion-exchange-Oxine (Gravimetric)	2.2%	Based on 12 determinations on synthetic 1 w/o Al alloy samples.
Ion-exchange-Oxine (Volumetric)	1.6%	Based on 17 determinations on synthetic 1 w/o Al alloy samples.
Ion-exchange-EDTA	2.0%	Based on 12 determinations on synthetic 1 w/o Al alloy samples.

synthetic alloy samples after the methods had been modified to eliminate nickel interference. The data are given in Table IV.

Comparison with other methods

It is possible to compare the precision of the procedures discussed in this report with the precision of the two other methods reported for determining aluminum in plutonium alloys[1,2]. Data for these are given in Table V.

SUMMARY

An anion-exchange method has been developed for the separation of aluminum from plutonium in a 1% aluminum–plutonium alloy. After separation, the aluminum is determined using oxine, either volumetrically or gravimetrically, or by a complexometric titration using EDTA. The volumetric methods are favored because they are faster. On synthetic alloy samples containing 5.00 mg of aluminum the mean recovery and the standard deviation of the volumetric oxine method are 4.93 mg and ± 0.08 mg, respectively. Using the EDTA procedure, the comparable values are 4.92 mg and ± 0.10 mg, respectively. Of the elements commonly present as impurities only nickel interferes, but the volumetric procedures can be modified so that this interference is eliminated.

RÉSUMÉ

Une méthode par échange d'anions est proposée pour la séparation de l'aluminium d'avec le plutonium. Après séparation, l'aluminium peut être dosé soit par volumétrie, soit par gravimétrie, à l'aide d'oxine; on peut également effectuer un dosage complexométrique au moyen de l'acide éthylènediaminotétracétique (EDTA). Parmi les éléments généralement présents comme impuretés, seul le nickel gêne; on peut éviter cette perturbation en modifiant les procédés volumétriques.

ZUSAMMENFASSUNG

Aluminium lässt sich von Plutonium mit Hilfe eines Jonenaustauschers trennen. Die Bestimmung des Aluminiums als Oxychinolat kann gravimetrisch, volumetrisch oder komplexometrisch mit Aethylendiaminotetraessigsäure erfolgen. Von den üblichen Verunreinigungen stört nur Nickel, dessen Einfluss durch eine modifizierte volumetrische Methode eliminiert werden kann.

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PYROMELLITEIN INDICATORS

II. ADSORPTION INDICATORS

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The first paper[1] of this series introduced a new group of indicators prepared from pyromellitic dianhydride by condensing four phenolic molecules with one molecule of the dianhydride. Among these are two which resemble fluorescein; one containing four resorcinol groups and the other containing two resorcinol and two phenol groups. Two additional indicators were prepared from these by bromination, in the same manner by which eosin is made from fluorescein. There were therefore four possible adsorption indicators to work with, which will be designated in this article as roman numerals as follows: I. Tetra-resorcinol pyromellitein; II. Diresorcinol diphenol pyromellitein; III. Brominated product of I. IV. Brominated product of II.

Preliminary tests had determined that the other indicators listed in the first paper did not adsorb on silver halide precipitates. At the start of the study being discussed here, it was determined that compound IV did not adsorb, and that compound II, from which it was prepared, adsorbed very weakly, it being necessary to use so much of this indicator that it was considered that the pink color on silver chloride might be due to impurity (compound I).

As a comparison method, it was decided to titrate the soluble halides using 0.1 N $AgNO_3$ by Fajans method[2], and to compare the results obtained with those using dichlorofluorescein. The effect of acidity was determined by adding 3 M HNO_3 to some solutions, and titrations in the presence of colored ions were carried out in 1 M HNO_3 solutions. Eosin was included for comparison purposes. The results of these experiments may be summarized as follows:

A. *For the titration of chlorides,* indicator I gives results identical with those obtained in neutral and slightly acid solutions using dichlorofluorescein, but indicator II gives poor results. For the chloride titration in more acid solutions, however, where dichlorofluorescein cannot be used, indicator II gives good results, even in the presence of highly colored ions such as Cr^{+3}, Fe^{+3}, Cu^{+2}, Ni^{+2}, and Co^{+2} in 1 M HNO_3. In the absence of colored ions an excellent end-point was obtained in an acidity as high as 1 M HNO_3.

B. *For the titration of bromides,* indicator II gave excellent results over a wide range of acidities, from neutral to 1 M HNO_3, while indicator I gave results similar to those of dichlorofluorescein with bromides.

C. *For the titration of iodides,* indicator II also gave excellent results over a wide range of acidities, while indicator I gave results similar to those of dichlorofluorescein with bromides.

D. *In titrating thiocyanate solution,* indicator II gave very good results both in dilute and strong acid, the end-points being sharp and the checks excellent. The color of colored thiocyanate ions (such as ferric), of course, interferes.

E. *In the titration of very dilute solutions of all three halides,* indicator I gave results at least as good as those obtained with dichlorofluorescein in weak acid solutions, while indicator II gave better results for bromides and iodides in weak acid solution, and very good results for all three halides in solutions of HNO_3 which were 0.05 M or stronger.

The good results obtained for bromides and iodides may be due to the fact that the color of indicator II on adsorption has a more purple tinge than that shown by dichlorofluorescein, eosin, and indicator I which are shades of pink when adsorbed. The color changes of indicators I and II are listed in Table I.

TABLE I

Indicator	*Acidity*	*Solution color*	*Adsorbed color*
Indicator I	Neutral	Green-Yellow fluorescence	Pink (coral)
Indicator II	Neutral	Pink	Purple
Indicator I	0.05 N	Yellow	Pink (not at equiv. pt.)
Indicator II	0.05 N	Orange	Purple
Indicator II	1 N	Orange	Purple (more pink)

All indicator solutions in these tests were made up by dissolving 0.1 g of indicator in 100 ml H_2O, one drop of 6 N NaOH being added to aid in dissolving the indicator.

When 0.1 N halide solutions were tested, five drops of indicator were used for a total final volume of about 50 ml. When very weak halide solutions were titrated, only one drop of indicator solution was used.

ACKNOWLEDGEMENT

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SUMMARY

Two new indicators have been made and tested, one of them being a substitute for dichlorofluorescein, the other showing excellent end-points in moderately strong nitric acid solutions for chlorides, bromides, iodides and thiocyanates even in the presence of colored ions.

RÉSUMÉ

Des indicateurs ont été préparés par condensation du dianhydride pyromellique avec le résorcinol. Ils ont été examinés en vue de leur emploi comme indicateurs d'adsorption.

ZUSAMMENFASSUNG

Die Reaktionsprodukte von Pyromellitsäure-dianhydrid mit Resorcin wurden auf ihre Eignung als Adsorptionsindikatoren untersucht.

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RAPID EXTRACTION OF IRON(III) WITH 2-THENOYL TRIFLUOROACETONE

DIRECT COLORIMETRIC DETERMINATION IN THE ORGANIC PHASE

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Various metal ions react with 2-thenoyltrifluoroacetone (TTA) to give chelates which are intensely colored, relatively stable, insoluble in aqueous solutions, but soluble in many organic solvents. BERG AND MCINTYRE[1] reported the paper chromatographic separation of mixtures of TTA-chelates with iron(III), cobalt(II), copper (II), nickel(II) and manganese(II), by means of the mixed solvent system, benzene, methanol and glacial acetic acid. They prepared iron(III)-TTA chelate and determined its molecular weight as 718.8 which indicates the formula $Fe(TTA)_3$. They also noted the absorption spectrum in ethyl alcohol. In an earlier report BOLOMEY AND WISH[2] observed that the equilibrium constant for the iron(III)-TTA complex exceeds 1 and that the optimum pH for extraction into benzene is around 2 to 3. They measured the ferric chelate in the benzene phase spectrophotometrically at 470 mμ. But systematic extraction and colorimetric studies of iron(III) with TTA are lacking.

In the present work the brilliant red color of the iron(III)-TTA complex in benzene has been utilised in a rapid spectrophotometric method for iron(III) at the milligram level. The various factors involved in the extraction and colorimetric measurement have been critically studied. A preliminary note of this work is under publication[3].

EXPERIMENTAL

Apparatus

A Hilger Quartz Spectrophotometer, with matched 1-cm quartz cells, was used for absorbance measurements; pH values were measured with a Cambridge pH meter.

Reagents

All the chemicals used, unless otherwise mentioned, were chemically pure or reagent grade materials.

Approximately 0.15 *M* solutions of TTA (Columbia organic chemicals, U.S.A.) (m.p. 42-43°) in benzene were used. More dilute solutions (*ca.* 0.01 *M*) were ineffective for rapid extractions.

A stock solution of iron(III) was prepared by dissolving about 4.5 g of ferric alum (Merck) in 500 ml of 5% sulphuric acid. The solution was standardized by permanganate titration. 1 ml of the solution contained 0.99 mg of iron. For the following studies the stock solution was diluted ten-fold so that the iron content was 99 μg per ml.

GENERAL PROCEDURE

A suitable aliquot (1 or 2 ml) of the diluted ferric alum solution was adjusted to pH 2.0 with 0.01 *N* hydrochloric acid and 0.01 *N* sodium hydroxide using the pH meter and then diluted with water to 25 ml. For pH studies, the solution containing iron was adjusted to different pH values and then diluted as above. For interference studies, the solution containing the desired ion was introduced before the pH was adjusted. The aqueous solution thus prepared was transferred to a 250-ml separatory funnel and shaken for 10 min with 10 ml of 0.15 *M* TTA solution in benzene. The aqueous layer was drained into a beaker and the benzene layer into a 25-ml volumetric flask. The aqueous layer was rinsed with 5 ml of benzene in the separatory funnel and the benzene layer collected as before. The combined red benzene extracts were finally diluted to 25 ml with benzene and the absorbance measured at 460 mμ against a reagent blank. The corresponding iron concentration was obtained from a calibration curve (see below).

RESULTS AND DISCUSSION

Absorption curve

Fig. 1 illustrates the absorption spectra of solutions containing no iron or $7.1 \cdot 10^{-5}$ *M* iron(III) treated as above. The bright red iron(III)–TTA system has a strong absorption below 400 mμ which gradually decreases and becomes negligible beyond 650 mμ. All absorbance measurements were made at 460 mμ. The molar extinction coefficient at 460 mμ is 4880 ± 61 (on the basis of iron content).

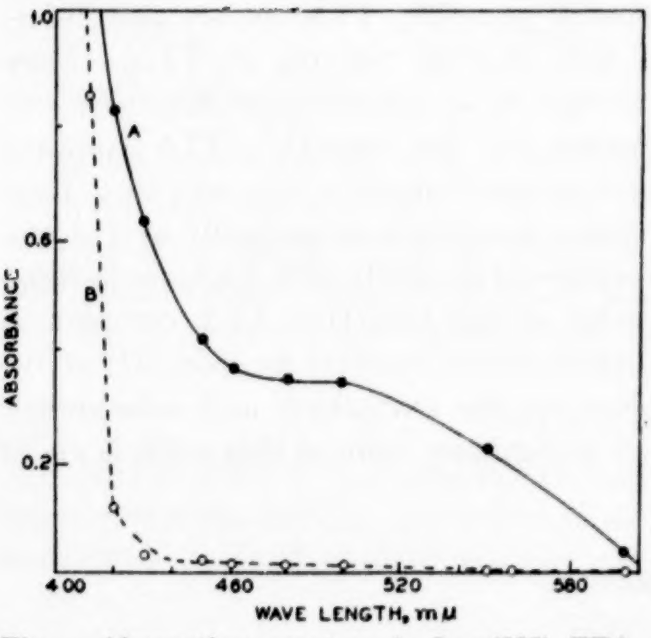

Fig. 1. Absorption spectra. A. Iron(III)–TTA complex in benzene against benzene as reference solution. Fe^{+3}, $7.1 \cdot 10^{-5}$ *M*; pH 2.0. B. Reagent blank against benzene, TTA, $15 \cdot 10^{-2}$ *M*; pH 2.0.

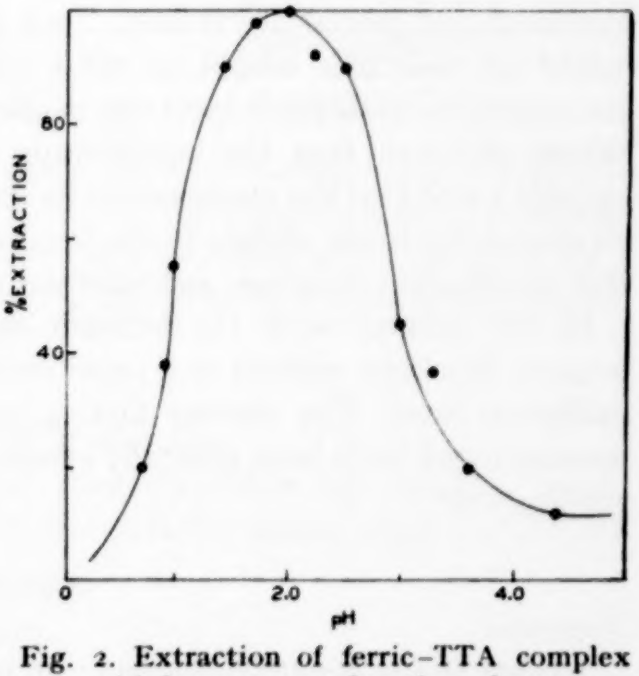

Fig. 2. Extraction of ferric–TTA complex with benzene as a function of pH.

Effect of pH

The extraction of iron(III) with TTA-benzene was investigated over the pH range 0.3–4.5. At higher pH the precipitation of ferric hydroxide causes trouble. The distribution constants, K_D, were calculated from extraction curves[4] (Table I). The optimum pH for 90% or more extraction is 1.5 to 2.7 which agrees fairly well with the pH range, *viz.* 2–3, predicted by BOLOMEY AND WISH[2], who used more dilute solutions of TTA (*ca.* 0.01 *M*) and extracted for several hours. At pH 2.0 quantitative extraction (100%; $K_D = a$) is observed (Fig. 2).

TABLE I

DISTRIBUTION CONSTANTS OF FERRIC-THENOYLTRIFLUOROACETONATE BETWEEN BENZENE AND AQUEOUS SOLUTION AS FUNCTION OF PH

pH	% *Iron extracted into benzene*	K_D
0.7	20	0.63
0.9	38	1.53
1.0	55	3.06
1.2	72	6.43
1.4	88	18.33
1.6	94	39.15
1.8	98	122.50
2.0	100	*a*
2.2	99	247.5
2.4	96	60
2.6	93	33.12
2.8	86	15.36
3.0	45	2.05
3.2	34	1.29
3.4	27	0.93
3.6	20	0.63
3.8	17	0.51
4.0	14	0.41
4.2	13	0.37
4.4	12	0.34

Calibration curve

Different amounts of iron (100, 150, 180 and 200 μg) were taken, and the absorbances measured at 450, 460 and 480 mμ against a reagent blank. Beer's law is obeyed at 460 mμ over a range of 1 to 10 μg iron per ml (Table II).

TABLE II

BEER'S LAW

Iron taken[a] μg	*Absorbance*		
	450 mμ	*460 mμ*	*480 mμ*
100	0.385	0.350	0.330
150	0.585	0.515	0.500
180	0.680	0.620	0.575
200	0.790	0.700	0.680

[a] Final volume of benzene solution was 25 ml containing the above amounts of iron.

Reagent concentration

The amount of TTA was changed from 0.008 *M* to 0.15 *M* while other factors were kept constant (Table III). The optimum concentration appears to be 0.15 *M*.

TABLE III

EFFECT OF REAGENT CONCENTRATION

200 μg of iron(III) gives an absorbance reading of 0.700 ± 0.008

TTA concentration (M)	*TTA added (ml)*	*Absorbance at 460 mμ*	*% extraction*
0.008	10	0.135	18.5
0.015	10	0.415	58.5
0.15	2	0.600	85.0
0.15	5	0.620	88.5
0.15	10	0.700	100
0.15	20	0.700	100

Stability of color

The absorbance of a solution of ferric–TTA complex (iron = 0.1 mg) was measured after 30 min, 2, 24, 48, 72, 96 and 168 h. The values obtained were 0.350, 0.352, 0.350, 0.345, 0.345, 0.345 and 0.335 respectively. The color was stable up to 96 h after which it underwent slow decomposition. At the end of 168 h the absorbance decreased by 4.3%.

Interfering ions

The following ions were taken through the procedure (iron = 0.2 mg): Ag^{+}, Cu^{+2}, Hg^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Bi^{+3}, Al^{+3}, Cr^{+3}, Ce^{+4}, Th^{+4}, Zr^{+4}, U^{+6}, PO_4^{-3}, citrate and tartrate (Table IV). Uranium, cerium, thorium, zirconium, copper,

TABLE IV

INTERFERING IONS

Iron(III) = 200 μg

Ion	*Concentration of ion (mg)*	*Added as*	*Absorbance at 460 mμ*	*Remarks*
None	—	—	0.700 ± 0.008	
Ag^{+}	20	$AgNO_3$	0.660	Interference
Cu^{+2}	21.3	$CuSO_4\cdot 5H_2O$	1.23	Color reaction
Hg^{+2}	21.3[a]	$HgCl_2$	0.705	No interference
Mn^{+2}	10	$MnSO_4\cdot 7H_2O$	0.560	Emulsion formed
Co^{+2}	20	$Co(NO_3)_2\cdot 6H_2O$	0.700	No interference
Ni^{+2}	21.5	$NiSO_4\cdot 7H_2O$	0.520	Interference
Bi^{+3}	0.5[b]	$BiOCl$	0.555	Interference
Al^{+3}	20	$Al_2(SO_4)_3\cdot 18H_2O$	0.680	Interference
Cr^{+3}	20	$Cr(NO_3)_3\cdot 9H_2O$	0.700	No interference
Ce^{+4}	25.6	$Ce(SO_4)_2\cdot 4H_2O$	0.98	Color reaction
Th^{+4}	26.2	$Th(NO_3)_4\cdot 4H_2O$	0.540	Interference
Zr^{+4}	1.0[c]	$ZrOCl_2\cdot 8H_2O$	0.550	Precipitation of zirconium chelate
U^{+6}	24.6	$UO_2(NO_3)_2\cdot 6H_2O$	0.940	Color reaction
PO_4^{-3}	20	$Na_2HPO_4\cdot 12H_2O$	0.210	Strong interference
Citrate	20	Citric acid	0.265	Interference
Tartrate	20	Tartaric acid	0.420	Interference

[a] Larger amounts interfere.

[b] Extraction is difficult with larger amounts owing to increased oxysalt formation.

[c] Zirconium in larger amounts is troublesome because of voluminous precipitation of zirconium chelate.

phosphate and citrate interfere seriously. Silver, nickel, manganese, bismuth, aluminium and tartrate also interfere. The ferric–TTA system (iron = 0.2 mg) can tolerate 20 mg amounts of mercury(II), cobalt(II) and chromium(III).

RECOMMENDED PROCEDURE

Take an aliquot containing 25 to 200 μg iron, adjust to pH 2.0 with 0.01 N hydrochloric acid and 0.01N sodium hydroxide with the help of a pH meter and transfer the solution (*ca.* 25 ml) to a 250-ml separatory funnel. Extract for 10 min with 10 ml of 0.15 M TTA–benzene solution. Allow the phases to settle, withdraw the aqueous layer into a beaker and the benzene layer into a 25-ml volumetric flask. Pour the aqueous solution back into the separatory funnel and rinse with 5 ml of benzene. Collect the benzene layer in the flask. Dilute the combined organic extracts to 25 ml with benzene. Measure the absorbance at 460 mμ against a reagent blank and calculate the iron concentration from the calibration curve.

TABLE V

ACCURACY OF THE PROPOSED METHOD

Iron taken μg	*Absorbance at 460 mμ*	*Iron found* μg	*% Error*
400[a]	0.695	398	−0.50
300[a]	0.522	302	+0.67
250[a]	0.395	252	+0.80
200	0.700	200	0.00
160	0.540	160	0.00
120	0.382	118	−1.60
100	0.345	99.5	−0.50

[a] The final volume of benzene solution was 50 ml.

To determine the accuracy of the method, known amounts of iron(III) were treated as above. The results (Table V) are accurate to within ± 1%. From six runs with 0.2 mg of iron(III), the absorbance found was 0.700 ± 0.008; the standard deviation was ± 1.14%. Thus the method enjoys good precision and accuracy. As little as 0.4 μg of iron per ml can be detected, which indicates the high sensitivity.

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SUMMARY

2-Thenoyltrifluoroacetone is investigated for the rapid extraction and spectrophotometric determination of iron(III) at the milligram level. The red extract absorbs strongly below 400 mμ. The color is stable for many hours; Beer's law is obeyed at 460 mμ for 1–10 μg of iron/ml. Interferences are studied. The method is reproducible to ± 1%.

RÉSUMÉ

La thénoyl-2-trifluoracétone est proposée comme réactif pour le dosage du fer(III). On peut ainsi effectuer une extraction rapide et une détermination spectrophotométrique directe du fer dans la phase organique.

ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Eisen(III) kann Thenoyltrifluoroaceton verwendet werden. Der gebildete Komplex ist Benzol-löslich. Die störenden Kationen und Anionen werden erwähnt.

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BEHAVIOUR OF BISMUTH NITRATE SPOTS IN INORGANIC PAPER CHROMATOGRAPHY

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In the course of a study of the chromatography of metal ions using butanol–water–thiocyanic acid as solvent, bismuth was found to give unusual crescent shaped spots.

EXPERIMENTAL

n-Butanol and aqueous 2.5 *N* thiocyanic acid (140:40) were mixed to give a single phase solvent, 0.53 *M* in thiocyanic acid. The chromatograms were prepared by the ascending technique of Williams and Kirby[1] using Whatman's No. 41 papers and were developed to a height of 15 to 18 cm without the appearance of an adsorption front. The paper used had a Tappi freeness[2] of 645 which corresponds[3] to a surface area of the order of 19 sq. metres per gram. The bismuth spots were located by treating the chromatograms successively with H_2S and NH_3 gases.

The bismuth solutions were in general 0.1 *M* in bismuth but varied in acid concentration. Where bismuth solutions of lower concentration were used these were made by diluting the 0.1 *M* solutions with acid of the appropriate concentrations. Five acids were used, nitric, perchloric, hydrochloric, hydrobromic and thiocyanic, and for the stock solutions the respective acid concentrations were 0.75 *M*, 0.6 *M*, 1 *M*, 0.5 *M* and between 1 and 2 *M* for the thiocyanic acid.

Approximately 0.005 ml of bismuth solutions was taken for each spot.

The perchlorate, thiocyanate and bromide solutions gave clear cut and slightly comet shaped spots at an R_F value of about 0.88. Solutions containing chloride and nitrate ions had R_F values of 0.45 and 0.65 respectively. These spots generally were of the shape shown in Fig. 1.

Varying the quantity of bismuth in the chloride (1 *M*) and nitrate (0.75 *M*) solutions from 10 to 100 μg per spot caused no significant change in either the R_F value of these groups or in the shape of the bismuth chloride spots. However, as the concentration of bismuth was varied from 0.1 *M* to 0.01 *M* so the lower portion of the bismuth nitrate spot tended to assume a more regular oval shape.

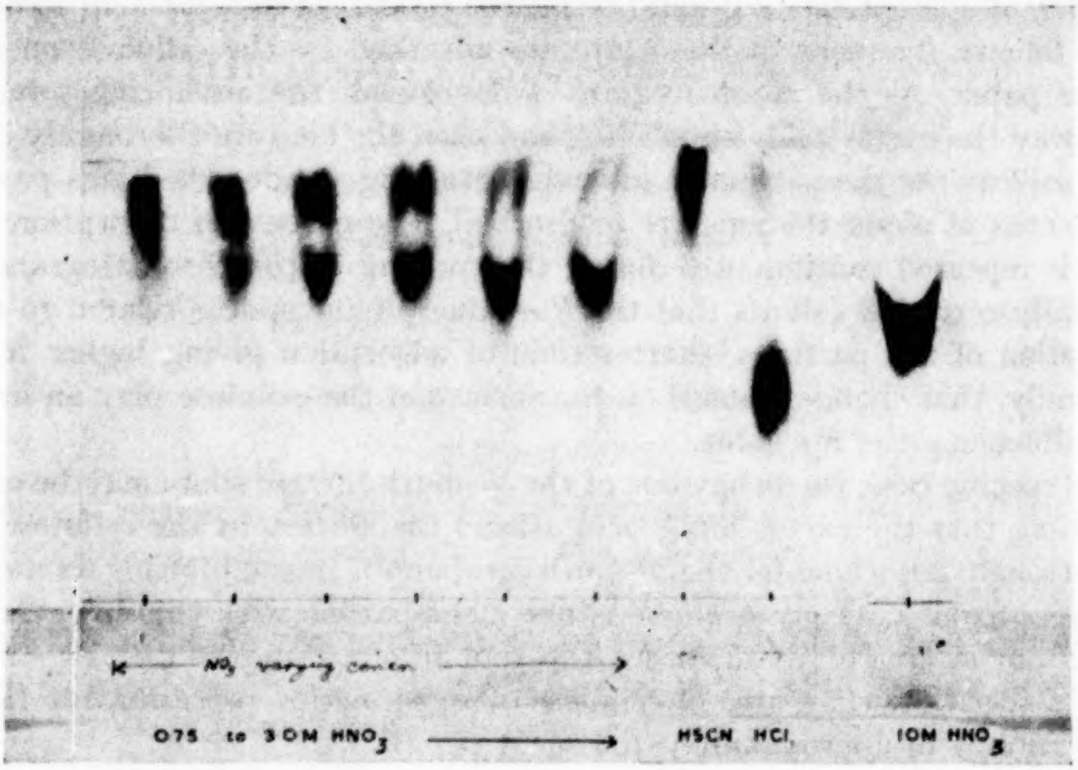

Fig. 1. Behaviour of $Bi(NO_3)_3$-spots in inorganic chromatography.

DISCUSSION

It might be expected that, of the five anions chosen, the chloride, bromide and thiocyanate bonds with bismuth would have a considerable degree of covalent character, while the nitrate and perchlorate link would be largely ionic. Whether bismuth in these latter was Bi^{+3} or BiO^{+} is not clear[4]. As MARTIN[5] has shown for antimony, bismuth as chloride and bromide may be expected to travel as covalent halides, $Bi(Ha)_3$ the thiocyanate may be of the same form or possibly Bi $(SCN)_6^{-3}$.

The bismuth chloride (except for a small amount), bromide and thiocyanate moved as colourless, pale buff and orange coloured spots respectively, at all times. The similarity between the R_F values for bismuth bromide and thiocyanate would appear to be incidental to this discussion. The bismuth chloride spot did furnish a bismuth thiocyanate spot amounting to 5–10% of the total bismuth. It appeared to be formed by a reaction between the developing solution and the spot material at the zone of the initial circular spot where its periphery and the horizontal interact. These two small spots travelled as bismuth thiocyanate, in some cases diffusing into one. In cases of mixed chloride and nitrate solutions, two systems of spots appeared, each system being characteristic for each ion.

The nitrate and perchlorate spots reacted with the developing solution as soon as it reached them but whereas the bismuth perchlorate travelled thereafter as thiocyanate to the normal position of the thiocyanate compound, the bismuth nitrate spot travelled in a hindered manner. This was due to the presence of a colourless spot of nitrate ion, oxidation product of nitrate and thiocyanate, or both, just ahead of it, and resulted in a variety of spot shapes, (Fig. 1.) and R_F values varying between 0.5 and 0.7 depending mainly on the acidity of the solution of bismuth nitrate. The higher acidities gave a spot area of 3.6 sq.cm.

The behaviour of the bismuth nitrate spot suggests that the process of development is one of adsorption. In general terms the process of development may be pictured as follows. The ions of the solute are adsorbed by the cellulose on spotting on to the paper. As the chromatogram is developed, the advancing solvent first washes away the excess acid, water, etc., and then the ions are thoroughly desorbed into the solvent. As the portion of solvent containing the desorbed ions passes over the fresh area of paper the ions are readsorbed. The process of desorption and adsorption is repeated continuously during the running of the chromatogram. If this is essentially correct it follows that the R_F values of the spot is related to the time of adsorption of the particles, shorter time of adsorption giving higher R_F value, and secondly, that changes caused on the surface of the cellulose play an important role in influencing the R_F value.

In this specific case, the behaviour of the bismuth nitrate spots may be explained by assuming that the excess nitric acid affects the surface of the cellulose making it more strongly adsorbing for the bismuth compound, thus inhibiting its movement.

The evidence of data given above is not incompatible with this hypothesis. Calculating from an area of 3.6 sq.cm for the spot of 0.005 ml of 0.1 M Bi^{+3} in nitrate solution, a specific surface area of cellulose of 19 sq.metres per gram for the paper, we have an area of approximately 200 sq. A per Bi^{+3}.

This does not seem excessive if we take into account that the bismuth is not distributed evenly over the spot; a factor of 3 may be assumed both up to and down from the average. Furthermore, the specific area of the cellulose refers to a determination made in water while the solvent discussed above is only of the order of 0.6 mol-fraction water, consequently the exposed surface area may be expected to be less.

SUMMARY

An investigation of irregularities found when chromatographing bismuth ions with butanol–water–thiocyanic solutions led to the conclusion that the process is one of absorption rather than partition for the development of this ion.

RÉSUMÉ

L'auteur a examiné le comportement du bismuth lors d'une étude de chromatographie sur papier d'ions métalliques, utilisant le mélange butanol–eau–acide thiocyanique comme solvant.

ZUSAMMENFASSUNG

Es wurde festgestellt, dass die bei der papier-chromatographischen Bestimmung von Wismut mit Butanol–Wasser–Thiocyanat beobachteten Unregelmässigkeiten auf Adsorptionserscheinungen zurückzuführen sind.

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SPECTROPHOTOMETRIC DETERMINATION OF NOBLE METALS WITH TIN(II) IN BROMIDE SOLUTIONS

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INTRODUCTION

The coloured products obtained from noble metals on treatment with tin(II) chloride have been used extensively for the colorimetric determination of these metals; but such reactions do not permit the determination of the metals in presence of one another. Recently, the reactions of rhodium[1] and iridium[2] with tin(II) bromide have been investigated. A broad study of all platinum metals has not hitherto been carried out, although a bromide medium appears to be very useful, since its sensitivity is greater than that of chloride.

In the present work we have examined from an analytical point of view the behaviour of platinum, rhodium, palladium, iridium and gold with tin(II) bromide, both in aqueous solutions and in organic solvents and extraction of the coloured products with isoamyl alcohol. The colours obtained are suitable for sensitive spectrophotometric determinations; it is possible also to perform several separations and simultaneous determinations. This work forms part of a wide investigation on noble metals which is being carried out in this Institute[3].

EXPERIMENTAL

Apparatus and solutions

Absorption measurements were made with a Beckman DU spectrophotometer, 1-cm Corex glass cells being used.

Reagent: 0.5 M $SnBr_2$ in 3 N HBr was prepared by dissolving pure tin in hydrobromic acid ($d = 1.48$) and diluting to the proper volume. Noble metals solutions in 0.2 N hydrobromic acid were prepared as follows:

Platinum: A suitable volume of standardized chloroplatinic acid solution was diluted with hydrobromic acid so that it contained 530 μg of Pt^{+4}/ml.

Rhodium: A solution containing 200 μg of Rh^{+3}/ml was made by dissolving $Na_3RhCl_6 \cdot 2\,H_2O$ in warm hydrobromic acid.

Palladium: $PdCl_2$ was dissolved in warm HBr to give a solution containing 576 μg of Pd^{+2}/ml.

Iridium: $IrCl_3$ was dissolved in warm HBr to give a solution containing 603 μg of Ir^{+3}/ml.

Gold: The metal was dissolved in aqua regia, evaporated almost to dryness and standardized gravimetrically. A solution containing 2 mg of Au^{+3}/ml was obtained by diluting a suitable volume of this solution with hydrobromic acid.

RESULTS

The optimal experimental conditions for the reaction between noble metals and stannous bromide were studied. The following results were obtained with pure solutions.

Platinum

The addition of reagent to a platinum(IV) solution caused a red colour to appear immediately and the colour was stable for several days. The absorption spectrum showed a peak at 463 mμ and the curve did not change on moderate heating of the solution. The optical density at the wavelength of the maximum was not affected by variations in the tin(II) concentration between 0.03 and 0.3 M. On increasing hydrogen ion concentration above 1 N the same spectral curves were obtained; at an acidity of less than 1 N no peak appeared. At 463 mμ Beer's law was followed strictly over the range 1 to 30 p.p.m. of platinum. The extinction coefficient was sufficiently high to provide a sensitive determination of this metal.

The colour was easily and completely extracted with isoamyl alcohol. The spectrum in this solvent, which was very similar to that obtained in aqueous solution, is shown in Fig. 1. The extracted colour was very stable and Beer's law was obeyed at 463 mμ; the determination could therefore also be done in isoamyl alcohol solution.

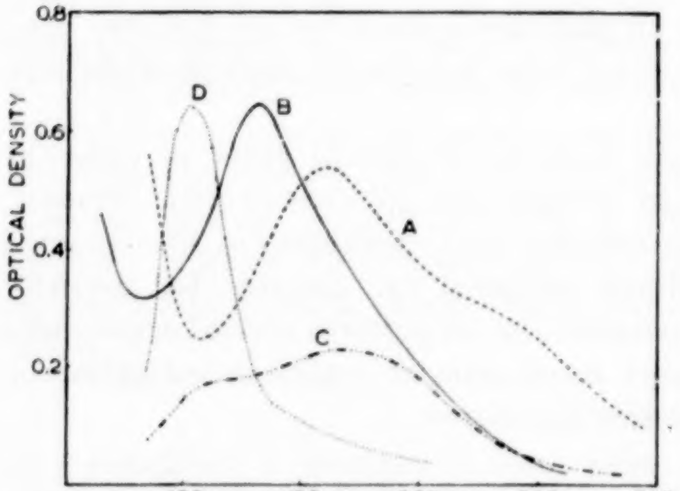

Fig. 1. Spectra in isoamyl alcohol: A. 10.6 μg Pt/ml. B. 2.3 μg Rh/ml. C. 10.1 μg Pd/ml. D. 6 μg Ir/ml.

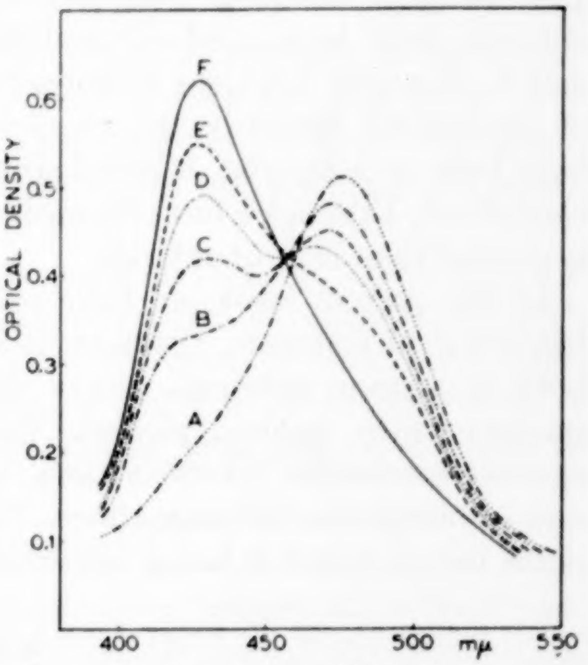

Fig. 2. Spectra of 2.3 μg Rh/ml with 0.5 M Sn(II) in 3 N HBr: A. after 6 min. B. 19 min. C. 44 min. D. 1 h. E. 1 h 30 min. F. 3 h 30 min.

Rhodium

When a rhodium(III) solution was mixed with the reagent at room temperature a red-orange colour first developed, its maximum being at 475 mμ in the spectral curve. After 1–2 hours the colour changed to yellow and a peak appeared at 427 mμ (Fig. 2). In solutions containing only hydrobromic acid the yellow colour was stable for only half an hour, but if perchloric acid was also added measurements could be made from 20–30 min to 2–3 h after mixing reagents; it was convenient to perfom all measurements at the same time in order to obtain good reproducibility. On gentle heating the yellow colour appeared in 2–3 min, but it was less stable than when obtained at room temperature and its optical density was lower. The optimal conditions were a tin(II) concentration of not less than 0.1 M and an acidity between 2.5 and 3 N (almost 50% of both HBr and $HClO_4$). Beer's law was followed at 427 mμ

from 0.1 to 5 p.p.m. of rhodium. The molar extinction coefficient was 3.10^4, hence the determination was very sensitive.

The yellow product could be extracted into isoamyl alcohol; the spectrum is shown in Fig. 1, the maximum lying at 429 mμ. When the extraction was made after the yellow colour had developed, the spectrum in the organic solvent did not change within 12 h. Beer's law was again followed. Thus rhodium can be determined in isoamyl alcohol as well as in aqueous solution.

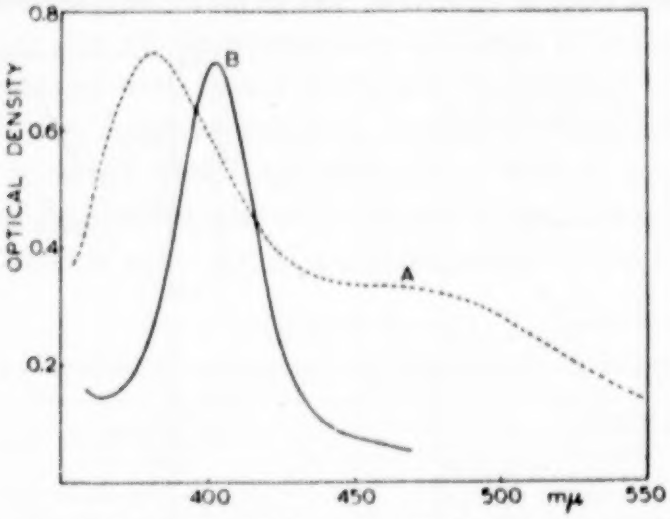

Fig. 3. Spectra in presence of 0.1 M Sn(II) and 3 N HBr: A. 10 μg Pd/ml. B. 5 μg Ir/ml.

Palladium

Palladium(II) gave a yellow-brown colour with tin(II) bromide. The spectrum is shown in Fig. 3; a peak at 385 mμ and a plateau in the range 440–460 mμ are noticeable. In view of the absorbance of tin-bromide complexes below 400 mμ, all measurements should be made on the plateau instead of at the maximum. The optical density was very sensitive to the concentrations of tin(II) and hydrogen ion. The optimal experimental conditions were an acidity of almost 3 M and a tin(II) concentration above 0.1 M. The colour was stable for only 1 h and Beer's law was followed from 1 to 10 p.p.m. With higher amounts of palladium, a calibration curve should be determined.

The yellow-brown colour was readily extracted by isoamyl alcohol. The spectrum in the organic solvent did not show a peak at 385 mμ, but only a rounded maximum at 450 mμ (Fig. 1). Since Beer's law was obeyed at this wavelength, a sensitive determination could be performed. The colour was more stable when perchloric acid was present in the aqueous solutions before extraction.

Iridium

No colour was observed on treating an iridium(III) solution with tin(II) bromide at room temperature for several days. A yellow colour developed on heating for some minutes[2]. The spectrum is shown in Fig. 3; the maximum optical density (at 403 mμ) and the greatest stability of the colour (several hours) were obtained with 0.1–0.2 M tin(II) bromide acidity of 2–3 N. The colour followed Beer's law and the useful range for determining iridium was 0.1 to 5 p.p.m.

Isoamyl alcohol could be used for extraction of solutions which were very high in hydrogen ion concentration. The spectrum obtained in this solvent is shown in Fig. 1. However, the results were not very reproducible and determinations should be done only in aqueous solutions.

Gold

The behaviour of gold with tin(II) bromide was very different from that of the other noble metals. Finely divided gold metal seemed to be produced; in the absence of protective colloids a blue-gray colour appeared which gave a black precipitate within an hour. When 0.05% gelatine was present as protective colloid, a stable reproducible violet colour was obtained which depended on the acidity of the solutions (Figs. 4 and 5). The concentration of stannous bromide should be greater than 0.05 *N* for rapid colour development, but it must be less than 0.15 *M* to avoid turbidity in solutions containing gelatine. Beer's law was obeyed between 540 and 550 mμ over the range 5 to 50 p.p.m. The colour could not be extracted with organic solvents.

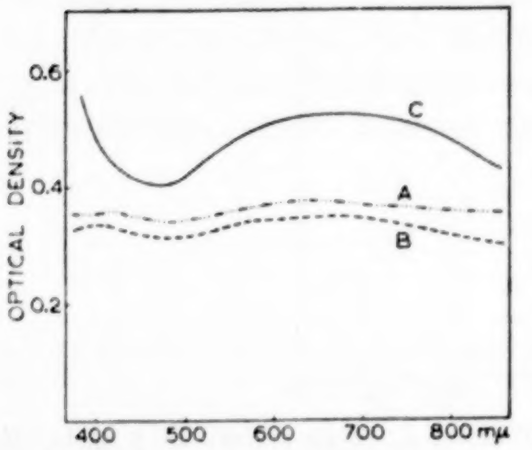

Fig. 4. Spectra of 40 μg Au/ml in presence of 0.05 *M* $SnBr_2$ without gelatine: A. H^+ = 1 *N*. B. H^+ = 2 *N*. C. H^+ = 6 *N*.

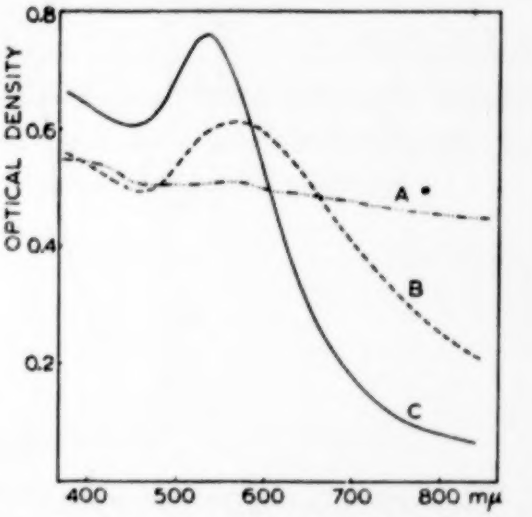

Fig. 5. Spectra of 40 μg Au/ml in presence of 0.05 *M* $SnBr_2$ with 0.05% gelatine: A. H^+ = 1 *N*. B. H^+ = 2 *N*. C. H^+ = 6 *N*.

The spectrophotometric data of the 5 elements investigated are summarized in Table I.

TABLE I

SPECTROPHOTOMETRIC DATA OF PLATINUM, RHODIUM, PALLADIUM, IRIDIUM AND GOLD IN PRESENCE OF TIN(II) BROMIDE

Metal	*Tin(II) concn. (M)*	*H^+ concn. (N)*	λ_{max}	*Molar extinction coefficient*	*Colour*
Pt	0.03–0.3	1	463	$9.3 \cdot 10^3$	red-orange
Rh	0.1	3	427	$3.0 \cdot 10^4$	yellow-orange
Pd	0.1	3	385	$6.7 \cdot 10^3$	yellow-brown
Ir	0.1 –0.2	2–3	403	$2.5 \cdot 10^4$	yellow[a]
Au	0.05–0.15	2	540	$3.2 \cdot 10^3$	violet[b]

[a] After heating for 3 min at 100°.
[b] In presence of 0.05% gelatine.

Separations and determinations of noble metals in presence of one another

The usefulness of the reactions with tin(II) bromide for the simultaneous determination of several noble metals was also studied.

a. Separation of gold from platinum metals. The formation of colloidal gold interferes seriously in the determinations of the other metals. Moreover, gold(III) in hydrobromic acid solutions is complexed as $HAuBr_4$. Since the dissociation of this complex is very small, it can be extracted by organic solvents such as ethyl ether, isoamyl alcohol, etc. Hence, gold should be extracted before the addition of tin(II) bromide; platinum metals are not extracted from hydrobromic acid solutions and remain in the aqueous phase so that they can be determined with tin(II) bromide.

b. Determination of platinum, rhodium and palladium in presence of iridium. As mentioned above, iridium does not react at room temperature, hence platinum, rhodium and palladium can be determined in presence of iridium, both in aqueous solutions and by extraction with isoamyl alcohol. Extraction is also advisable when iridium, which remains in aqueous solution, has to be determined. Some examples of determinations in presence of a large amount of iridium are shown in Table II; the coloured products were extracted with 25 ml of isoamyl alcohol from solutions containing 1 *N* hydrobromic acid, 1.5 *M* perchloric acid and 0.15 *M* tin(II) bromide.

TABLE II

DETERMINATION OF PLATINUM, RHODIUM AND PALLADIUM IN PRESENCE OF IRIDIUM

Metal (µg/ml)	*Wavelength (mµ)*	*Optical density*	
		Without Ir	*48.2 Ir µg/ml added*
Pt 8.5	463	0.428	0.434
Rh 2.4	429	0.580	0.571
Pd 9.2	450	0.365	0.366

c. Separation of platinum and rhodium from palladium. Several complex-forming substances can be used to eliminate palladium from a solution containing platinum and/or rhodium. Dimethylglyoxime forms a characteristic complex with palladium which can be used to precipitate this element[4]. But we have found that at acidities of 2 or 3 *M*, the results are better with α-nitroso-β-naphthol (or α-nitro-β-naphthol). Palladium is complexed by this ligand preferentially to platinum and rhodium. The complex can then be extracted with isoamyl alcohol and the other metals can be determined in the aqueous solution with tin(II) bromide. The results are rather low and errors of 5–7% can be expected.

d. Simultaneous determination of rhodium and platinum. It is not easy to extract or mask either of these elements when the other is present. However, it is possible to use the wavelengths corresponding to maxima in the spectrum of each. In solutions which are 1 *N* in hydrobromic acid, 1.5 *M* in perchloric acid and 0.15 *M* in tin(II) bromide, the optical density of platinum at 427 mµ is 51.5% of the density at 463 mµ; the optical density of rhodium at the latter wavelength is 59.5% of the density at 427 mµ. After the absorbances at these two wavelengths have been measured, the following equations must be solved:

$$D^{427}_{\text{total}} = D^{427}_{\text{Rh}} + 0.515\, D^{463}_{\text{Pt}}$$

$$D^{463}_{\text{total}} = D^{463}_{\text{Pt}} + 0.595\, D^{427}_{\text{Rh}}$$

In this way, the unknown D^{427}_{Rh} and D^{463}_{Pt} can be calculated and the amount of rhodium and platinum can be determined by comparison with a calibration curve. The results of some determinations by this method are shown in Table III.

TABLE III

SIMULTANEOUS DETERMINATION OF PLATINUM AND RHODIUM

Rh present µg	*Pt present* µg	D_{427}	D_{468}	*Rh found* µg	*Pt found* µg
40.6	53	0.465	0.347	40.5	53.5
40.6	106	0.516	0.441	40.8	102.7
40.6	159	0.562	0.547	39.8	161
40.6	212	0.620	0.649	40.5	213
20.3	53	0.263	0.230	20.5	55.6
20.3	106	0.312	0.329	20.2	108.5
20.3	159	0.367	0.434	20.4	163
20.3	212	0.420	0.534	20.6	215

ACKNOWLEDGEMENTS

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SUMMARY

In presence of tin(II) bromide, noble metals give coloured products which are suitable for spectrophotometric determinations. The colours are: red (platinum), yellow-orange (rhodium), yellow-brown (palladium), yellow (iridium) and violet (gold). They are extracted, except for gold, with isoamyl alcohol. Platinum, rhodium and palladium can be separated from iridium, and rhodium and platinum from palladium. Rhodium and platinum can be determined simultaneously.

RÉSUMÉ

Les métaux nobles réagissent avec le bromure d'étain(II), en solution bromhydrique, pour donner des produits diversément colorés. On a pu ainsi établir des méthodes de séparation et de dosage spectrophotométrique de ces éléments.

ZUSAMMENFASSUNG

Die Edelmetalle geben mit Zinn(II)-bromid in bromwasserstoffsaurer Lösung verschieden gefärbte Reaktionsprodukte, die sich zur Trennung und spektrophotometrischen Bestimmung dieser Metalle verwenden lassen.

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Anal. Chim. Acta, 22 (1960) 231–236

ZINC ACETATE AS A REAGENT IN GRAVIMETRIC ANALYSIS. I.

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In an earlier publication[1] it was shown that the precipitation of some anions of the second group by means of zinc acetate is quantitative and provides a satisfactory means of separating these anions. As many of the separations thus accomplished cannot be done easily by other gravimetric methods, the method has been investigated for the determination of these anions when they are present together in solution. It has been shown that zinc acetate gives satisfactory separations and permits the determination of anions in certain combinations which cannot be easily analysed otherwise.

For example, in the determination of iodide in presence of arsenate and selenite, the acidification of the solution liberates iodine with the reduction of arsenate and selenite. In the analysis of mixtures of phosphite and iodide, phosphite interferes with the estimation of iodide owing to the reduction of silver nitrate to metal. In the determination of iodide in presence of tellurite and tellurate, complexes are formed on acidification. All these difficulties can be overcome by the use of zinc acetate for separation.

Precipitation as Re_2S_7 is the most accurate method for the determination of rhenium but it cannot, of course, be used for its separation from metals such as arsenic, tellurium, etc., which also form thiosalts and are precipitated as sulphides. A preliminary separation by means of zinc acetate in presence of sodium carbonate permits the sulphide method to be used for the determination of these elements when present together.

EXPERIMENTAL

Determination of iodide in presence of arsenate, phosphite, selenite, tellurite or tellurate.

Measured volumes of standard solutions of sodium arsenate, sodium phosphite, potassium selenite, potassium tellurite, and potassium tellurate were made alkaline with sodium carbonate (0.5 g), mixed with a measured volume of a standard solution of potassium iodide and then treated with zinc acetate solution until no further precipitation occurred. The sodium carbonate was added to prevent the interaction of acids in neutral or acid solution and also to form zinc carbonate which simplified the filtration of the gelatinous precipitates obtained with zinc acetate. The mixture was heated nearly to boiling, digested on a hot plate for 10–15 min, cooled, filtered and washed thoroughly with distilled water.

The precipitate of the zinc salt was dissolved in dilute hydrochloric acid and the arsenate, selenite, tellurite and tellurate were estimated as sulphides[2,3]; the sodium sulphide was added after the acid present had been neutralized. The precipitate obtained with phosphite was dissolved in dilute nitric acid; the phosphite was oxidised to phosphate with an excess of permanganate (the excess being removed by addinga crystal of potassium nitrate) and determined as ammonium phosphomolybdate. In the filtrate from the zinc salts iodide was determined volumetrically using eosin as adsorption indicator or gravimetrically as silver iodide.

30–38 mg of arsenic were separated from 61–76 mg of iodine; 59–60 mg of selenium were separated from 61–76 mg of iodine; 44–55 mg of tellurium(IV) were separated from 61–76 mg of iodine; 57–65 mg of tellurium(VI) were separated from 61–76 mg of iodine; 3 mg of phosphite were separated from 61–76 mg of iodine.

The metals were recovered with an accuracy of:

As	= −0.2% to +0.3%	I = −0.3% to +0.2%
Se	= −0.3% to +0.4%	I = −0.2% to +0.1%
Te(IV)	= −0.2% to +0.3%	I = −0.2% to +0.25%
Te(VI)	= 0.0% to +0.25%	I = −0.1% to +0.25%
P	= −0.25% to +0.3%	I = −0.2% to +0.1%

Determination of rhenium in presence of arsenate, tellurate and tellurite.

Measured volumes of standard solutions of sodium arsenate, potassium tellurite or potassium tellurate were mixed with a measured volume of a standard solution of potassium perrhenate, made slightly alkaline with sodium carbonate (0.5 g) and treated as above. The precipitate of the zinc salt was dissolved in dilute hydrochloric acid, and the arsenate, tellurite and tellurate were determined as sulphides[2,3]. The filtrate from the zinc salt was made slightly acidic with dilute hydrochloric acid and concentrated to about 50 ml, and rhenium was also determined as sulphide[4].

30–38 mg of As were separated from 37–41 mg of rhenium; 44–55 mg of Te(IV) were separated from 37–41 mg of rhenium; 57–65 mg of Te(VI) were separated from 37–41 mg of rhenium.

The metals were recovered with an accuracy of:

As = -0.2% to $+0.35\%$ Re = -0.2% to $+0.3\%$
Te(IV) = -0.2% to $+0.3\%$ Re = -0.25% to $+0.4\%$
Te(VI) = 0.0% to $+0.3\%$ Re = -0.2% to $+0.3\%$

ACKNOWLEDGEMENT

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SUMMARY

Zinc acetate can be used for the gravimetric separation of iodide from arsenate, selenite, phosphite, tellurate and tellurite, and rhenium from arsenate, tellurate and tellurite.

RÉSUMÉ

L'acétate de zinc peut être utilisé pour la séparation gravimétrique des iodures d'avec les arséniates, sélénites, phosphites, tellurates et tellurites, et du rhénium d'avec les arséniates, tellurates et tellurites.

ZUSAMMENFASSUNG

Es wird gezeigt, dass mit Hilfe von Zinkacetat eine gravimetrische Trennung der Jodide von Arsenaten, Seleniten, Phosphiten, Telluraten und Telluriten sowie des Rheniums von Arsenaten, Telluraten und Telluriten erzielt werden kann.

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MASS-SPECTROMETRIC STUDY OF NITROGEN COMPOUNDS FROM PETROLEUM DISTILLATES*

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INTRODUCTION

Little detailed information is available on the type distribution of the nitrogen compounds in oil. Accordingly, characteristic petroleum distillates were subjected to careful fractionated distillations and chromatographic separations. Among the fractions obtained were basic and non-basic nitrogen concentrates having molecular weights from 220 to about 320.

In this paper a detailed description is given of the mass-spectrometric method which was developed to determine the type distribution of the compounds in the basic nitrogen concentrates. This includes the pyridine-quinoline type distribution and the subdistribution according to naphthenicity. In addition, some data are presented on basic nitrogen–sulphur compounds which were found to the present in the corresponding extracts.

MASS-SPECTROMETRIC DETERMINATION OF THE PYRIDINE-QUINOLINE TYPE DISTRIBUTION

Qualitative considerations

In concentrates of the type mentioned in the introduction the heteroaromatic nitrogen compounds that must be considered primarily are the pyridines and the (iso)quinolines. As naphtheno-aromatics – *e.g.* indanes and tetralins – are known to constitute an appreciable part of the aromatic hydrocarbons of similar molecular weight occurring in oil fractions the presence of mono- and dinaphthenopyridines along with alkylpyridines and of the corresponding quinolines should be reckoned with. Hence a mass-spectrometric method is required that is capable of determining not only the alkyl-substituted heteroaromatics but also their various naphtheno-substituted relatives. As will shortly be seen, this naphtheno-substitution necessitates the separate analysis of basic and non-basic nitrogen concentrates.

By analogy with aromatic hydrocarbons the various heteroaromatic nitrogen compounds are expected to show marked parent peaks, fragment peaks and/or rearrangement peaks at m/e-series corresponding to their molecular Z number** as well as to Z—1.

The parent ions of alkyl-, mononaphtheno- and dinaphthenopyridines have Z-values —5, —7 and —9, respectively; the corresponding quinolines have Z-numbers —11, —13 and —15, respectively.

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* Presented at the Seventh Annual ASTM-E14 Meeting on Mass Spectrometry, Los Angeles 1959

** Z is defined by the molecular formula $C_nH_{2n+Z}N$ and is a measure of the hydrogen deficiency.

Similarly the non-basic nitrogen compounds like alkyl-, mononaphtheno- and dinaphtheno-indoles or carbazoles have Z-values —9, —11 and —13 or —15, —17 and —19, respectively. Hence, dinaphtheno-pyridines and alkyl-indoles, alkylquinolines and mono-naphtheno-indoles, and other pairs appear indistinguishable as regards their Z-number.

As seen from the mass spectra[*] reproduced in Fig. 1, the basic heteroaromatic nitrogen compounds are indeed clearly characterized by their Z-numbers:

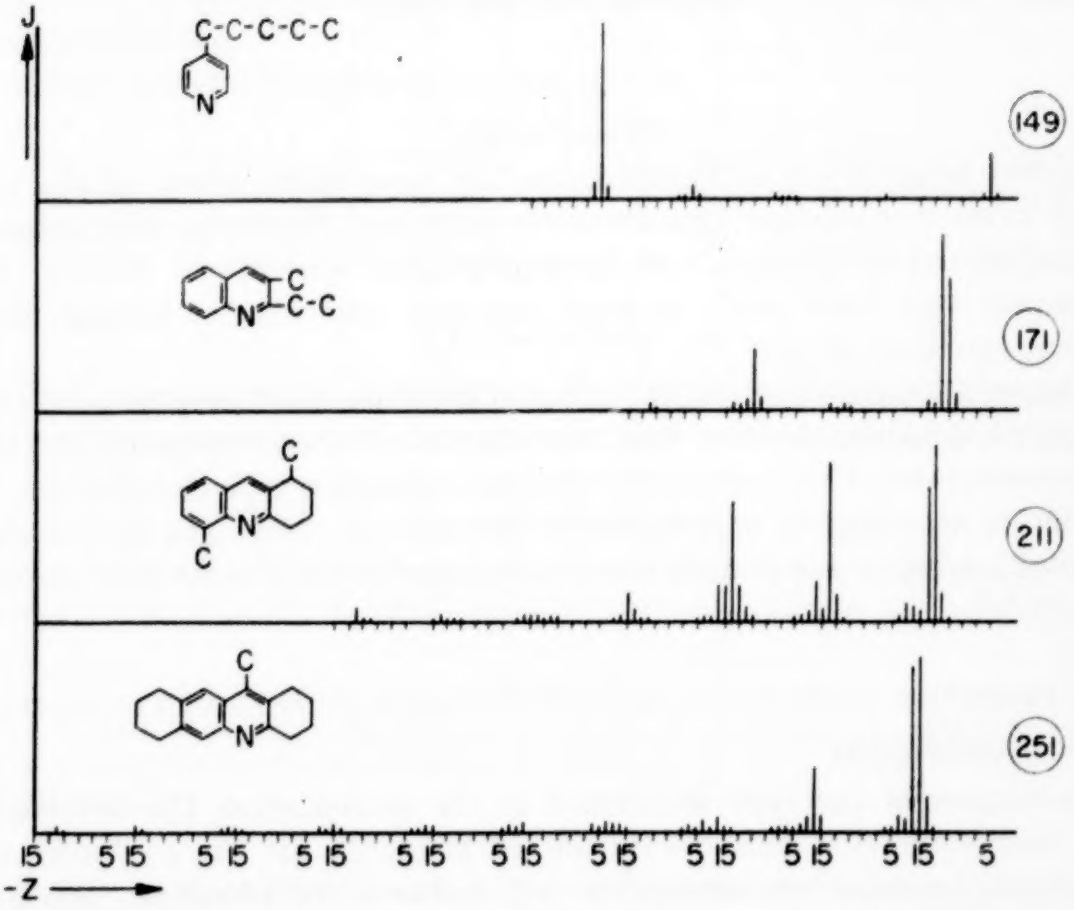

Fig. 1. Mass spectra of some basic nitrogen compounds. J = intensity in arbitrary units. The numbers at the right indicate the molecular weight. The spectra have been shifted horizontally with respect to each other by an integral multiple of 14 m/e units.

The strongest peaks of n-amylpyridine (Z = —5) appear at the mass/charge ratio: $m/e = 93$ (rearrangement peak) and at $m/e = 149$ (molecule ion) both belonging to the Z = —5 series; similarly methylethylquinoline (mol. wt. 171, Z = —11) has its major peaks confined to Z = —11 and Z = —12 positions; with the mononaphtheno-dimethylquinoline (mol. wt. 211, Z = —13) the major peaks are at Z = —13 and Z = —14 whereas with dinaphtheno-methylquinoline (mol. wt. 251, Z = —15) the strongest peaks are at Z = —15 and Z = —16 positions.

The mass spectra of these compounds and of others not given here are characterized by the following features:

(a) their base peak and other major peaks are found at series corresponding to Z and Z—1 if their molecular formula is given by $C_nH_{2n+z}N$.

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[*] Obtained with a Consolidated Model 21-103 C instrument, modified for high mass operation.

(b) the molecule ion peak is not necessarily the base peak but the latter and the other major peaks are found in the proper Z and $Z-1$ series down to the corresponding complete naphtheno-aromatic ring system without alkyl substituents.

Thus alkylpyridines as a class ($Z = -5$) are characterized by appreciable intensity in the sum S_1 of the ion currents at m/e values $\begin{matrix}78\\79\end{matrix} + i \times 14$. Mononaphthenopyridines would contribute mainly at m/e values $\begin{matrix}118\\119\end{matrix} + i \times 14$, sum S_2; as the first members of this class and of those of higher naphthenicity those with the maximum number of polycondensed five-membered rings for a given number of substituent C-atoms were chosen. The same applies to the quinoline classes starting with alkylquinolines ($Z = -11$) with the ion current sum (S_4) at m/e values $\begin{matrix}128\\129\end{matrix} + i \times 14$ and so on. Relevant data and symbols are given in Table I.

TABLE I

Py	*Q*	*Peak series*	*Intensity sum*	*Z-number*
0 *n* +	(4 *n*)	$\left.\begin{matrix}78\\79\end{matrix}\right\} + i \times 14$	S_1	-5
1 *n*		$\left.\begin{matrix}118\\119\end{matrix}\right\} + i \times 14$	S_2	-7
2 *n*		$\left.\begin{matrix}144\\145\end{matrix}\right\} + i \times 14$	S_3	-9
(3 *n*) +	0 *n*	$\left.\begin{matrix}128\\129\end{matrix}\right\} + i \times 14$	S_4	-11
	1 *n*	$\left.\begin{matrix}154\\155\end{matrix}\right\} + i \times 14$	S_5	-13
	2 *n*	$\left.\begin{matrix}180\\181\end{matrix}\right\} + i \times 14$	S_6	-15
	3 *n*	$\left.\begin{matrix}206\\207\end{matrix}\right\} + i \times 14$	S_7	-17

Ring systems (*Py* = pyridine, *Q* = quinoline, *n* = naphthenic ring), with corresponding peak series, intensity sums and *Z*-numbers.

Quantitative aspects

Once the characteristic peak sequences S_i have been selected the matrix for determining the pyridines and quinolines according to their Z-number should be devised; the choice of the S_i's described above already makes the diagonal elements s_{ii} the largest of each column.

The formal matrix is given in Table II. The matrix elements s_{ij} in each column j are to be obtained — except for a sensitivity factor — from model compounds. Intercomparability of columns — elimination of the sensitivity factor — can be obtained from total-ion-current (T_j) considerations and from data on synthetic blends of type concentrates: to the latter end a synthetic mixture of a pyridines concentrate (B91) and a quinolines concentrate (K76) — both having an average molecular weight of 231 — has been employed.

Let us first consider the intercomparability of columns. As shown by OTVOS AND STEVENSON[1] the total cross-sections of molecules for ionization under electron bombardment are additive in the cross-sections of the constituent atoms.

With the known atomic cross-sections of H, C and N the total molar cross-sections and hence the respective total molar ion currents Tm_1 and Tm_4 of an alkylpyridine

TABLE II

FORMAL MATRIX

	Py_{0n}	Py_{1n}	Py_{2n}	Q_{0n}	Q_{1n}	Q_{2n}	Q_{3n}
$-Z$	5	7	9	11	13	15	17
j	1	2	3	4	5	6	7
S_1	s_{11}	s_{12}	s_{13}	s_{14}	s_{15}	s_{16}	s_{17}
S_2	s_{21}	s_{22}	s_{23}	s_{24}	s_{25}	s_{26}	s_{27}
S_3	s_{31}	s_{32}	s_{33}	s_{34}	s_{35}	s_{36}	s_{37}
S_4	s_{41}	s_{42}	s_{43}	s_{44}	s_{45}	s_{46}	s_{47}
S_5	s_{51}	s_{52}	s_{53}	s_{54}	s_{55}	s_{56}	s_{57}
S_6	s_{61}	s_{62}	s_{63}	s_{64}	s_{65}	s_{66}	s_{67}
S_7	s_{71}	s_{72}	s_{73}	s_{74}	s_{75}	s_{76}	s_{77}
$\sum_i s_{ij}$	77	76	75	75	74	73	72

For the explanation of the $\sum_i s_{ij}$-values see text.

like $C_{17}H_{29}N$ (mol.wt. 247) and an alkylquinoline like $C_{18}H_{25}N$ (mol.wt. 255) are found to be 103.5 and 103.7, respectively, in arbitrary units. For the ratio of their "specific" total ion currents T_1 and T_4 — defined as total ion current per unit vapour density — follows $T_4/T_1 = 0.97$. This compares reasonably with the ratio $T_Q/T_{Py} = 1.01$ found experimentally with the synthetic blend (45.2% Py + 54.8% Q) of actual concentrates.

Accepting the T-values predicted for the successive Z-classes as correct, T_j would be 100, 99, 98, 97, 96, 95 and 94 in arbitrary units for $j = 1$ through $j = 7$, respectively, and for molecular weights around 250.

The next step is to ascertain what fraction f_j of T_j is present in the combined ion currents of the m/e series S_1 through S_7, in others words to find the quantity:

$$f_j = \sum_i s_{ij}/T_j.$$

To this end the f-values obtained from a variety of mass-spectra as given in Table III for mono(hetero)aromatics and in Table IV for di(hetero)aromatics may be considered. Some literature data on benzenes and naphthalenes — obtained on similar instruments — have been included in order to obtain a better balanced appreciation without making use of further model compounds.

The f-values increase with molecular weight: starting from $f \simeq 0.5$ for the low-molecular-weight members of the series an f-level of about 0.75 is approached in the C_{18}-region (mol.wt. $\approx$ 250) regardless of the Z-number of the molecular species. This further substantiated by the actual pyridine and quinoline concentrates which — despite a Z-difference of about 6 units — have almost identical f-values, *viz.* 0.77_5 and 0.79_2. In view of this near-identity, f_1 through f_7 will all be taken equal to 0.77 so that the sums of matrix elements per column $\sum_i s_{ij}$ attain the values given underneath the formal matrix (Table II).

Now the actual matrix elements s_{ij} per column j must be estimated from the mass patterns of model compounds and adjusted to give the proper $\sum_i s_{ij}$ value. Typical data are presented in Tables V and VI for mono- and di(hetero)aromatic compounds, respectively. From these the average s_{ij}-values for the final matrix are obtained: the columns s_{i3} and s_{i7} are estimated by inter- or extrapolation.

TABLE III

FRACTIONAL ION CURRENTS f_j OF MONO(HETERO)AROMATICS

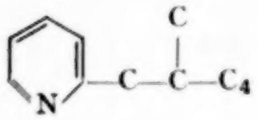
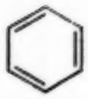
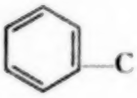
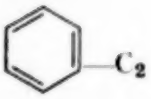
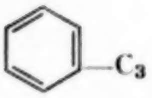
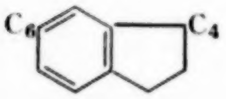
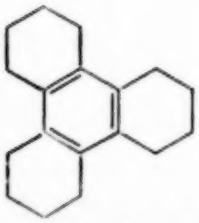
Compound	*Z-number*	*Molecular weight*	f_j
	—5	177	0.68_5
	(—6)	78	0.51
	(—6)	92	0.57
	(—6)	106	0.64
	(—6)	120	0.68
	(—8)	258	0.71
	(—12)	240	0.72
Pyridine concentrate B91	{—5 —7}	231	0.77_5

TABLE IV

FRACTIONAL ION CURRENTS f_j OF DI(HETERO)AROMATICS

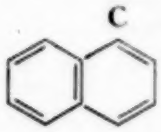
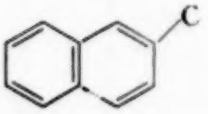
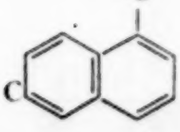
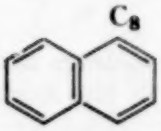
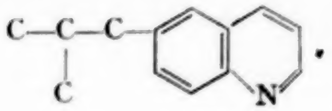
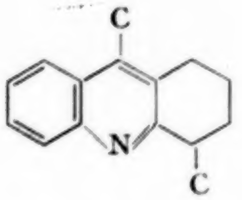
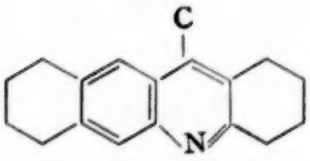
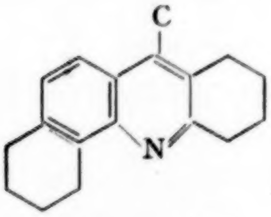
Compound	*Z-number*	*Molecular weight*	f_j
	(—12)	142	0.53
	(—12)	142	0.50
	(—12)	156	0.65
	(—12)	240	0.74

TABLE IV (continued)

	—11	185	0.62
	—13	211	0.69_3
	—15	251	0.70_3
	—15	251	0.75_3
Quinoline concentrate K76	{—11 —13}	231	0.79_2

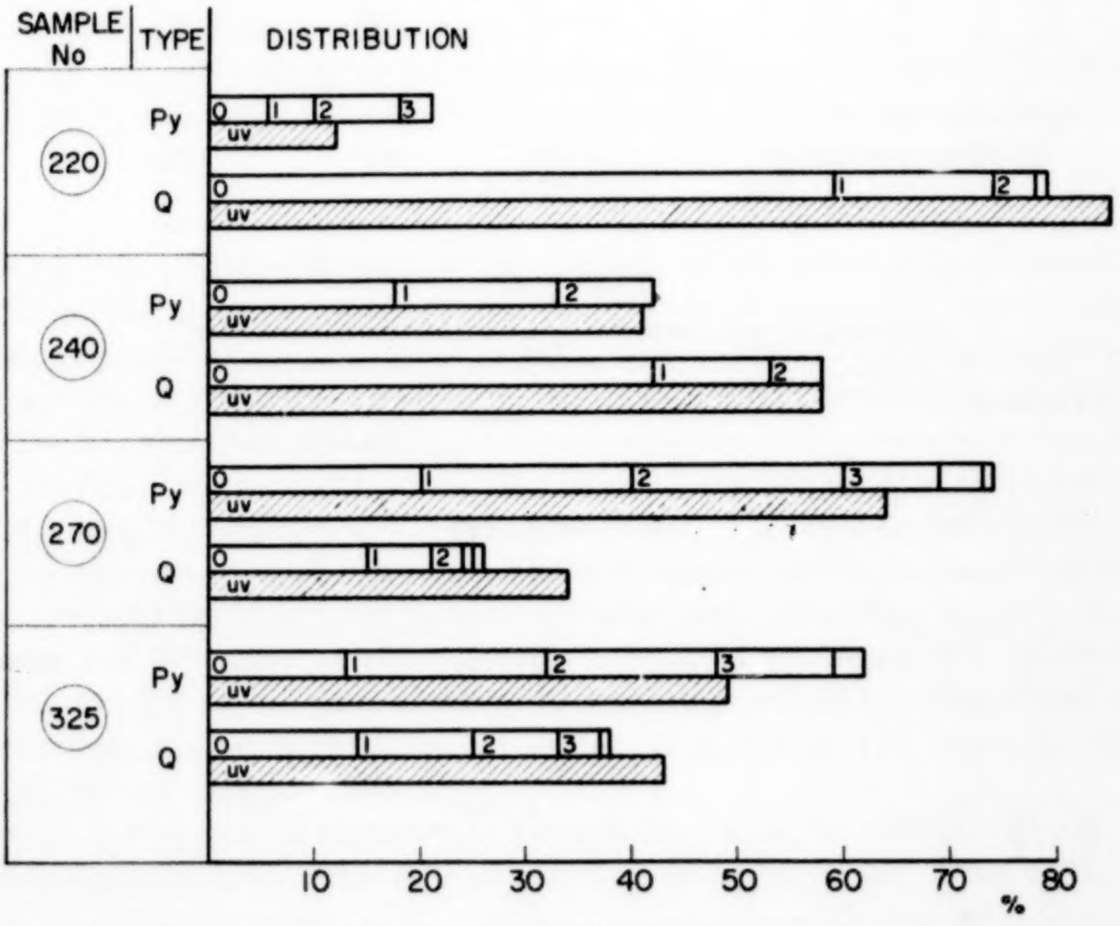


Fig. 2. Type distribution of pyridines and quinolines in four petroleum distillates according to mass-spectrometric and ultraviolet-spectroscopic analysis (u.v.) The figures in the horizonal bars indicate the number of naphthenic rings per molecule.

TABLE V

s_{ij} PATTERNS OF MONO(HETERO)AROMATICS

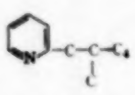
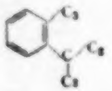
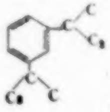
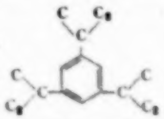
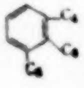
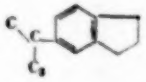
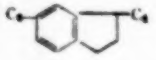
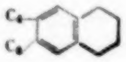
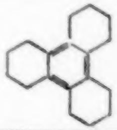
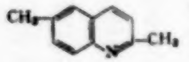
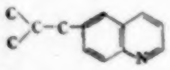
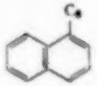
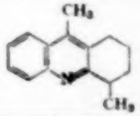
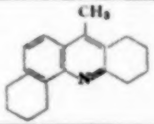
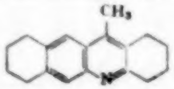
Class	*Alkylpyridines (benzenes)*						*Mononaphtheno compounds*				*Dinaphtheno compounds*	*Trinaphtheno compounds*
Compound						"Average"				"Average"	"inter-polated"	
Molecular weight	177	190	190	246	288		202	258	272			240
—z	5	(6)	(6)	(6)	(6)		(8)	(8)	(8)			(12)
j	1	1	1	1	1	1	2	2	2	2	3	
s_{1j}	$\underline{74}$	$\underline{68}$	$\underline{68}$	$\underline{68}$	$\underline{58}$	$\underline{65}$	8	9	7	7	2	2
s_{2j}	3	6	6	5	13	8	$\underline{62}$	$\underline{57}$	$\underline{56}$	$\underline{59}$	10	2
s_{3j}	—	1	1	1	1	1	5	6	7	6	$\underline{53}$	13
s_{4j}	—	2	2	1	3	2	1	4	6	4	6	$\underline{47}$
s_{5j}	—	—	—	—	—	—	—	—	—	—	2	8
s_{6j}	—	—	—	—	—	—	—	—	—	—	2	2
s_{7j}	—	—	—	2	2	1	—	—	—	—	0	1

TABLE VI

s_{ij} PATTERNS OF CONDENSED DI(HETERO)AROMATICS

Class	*Alkylquinolines (naphthalenes)*				*Mononaphtheno compounds*	*Dinaphtheno compounds*			*Trinaphtheno compounds*
Compound				"Average"				"Average"	Estimated
Molecular weight	157	185	240		211	251	251		250
—z	11	11	(12)		13	15	15	15	17
j	4	4	4	4	5	6	6	6	7
s_{1j}	—	2	1	1	2	4	4	4	10
s_{2j}	—	1	1	1	1	2	2	2	3
s_{3j}	7	3	4	5	0	1	1	1	2
s_{4j}	$\underline{68}$	$\underline{56}$	$\underline{65}$	$\underline{59}$	8	1	1	1	0
s_{5j}	—	12	4	9	$\underline{51}$	7	6	7	2
s_{6j}	—	1	0	0	11	$\underline{50}$	$\underline{51}$	$\underline{50}$	10
s_{7j}	—	—	—	—	1	7	8	8	$\underline{45}$

The resulting final s_{ij}-matrix is given in Table VII

TABLE VII

FINAL s_{ij}-MATRIX

−*Z* *j*	*5* *1*	*7* *2*	*9* *3*	*11* *4*	*13* *5*	*15* *6*	*17* *7*
S_1	$\underline{65}$	7	2	1	2	4	10
S_2	8	$\underline{59}$	10	1	1	2	3
S_3	1	5	$\underline{53}$	5	0	1	2
S_4	2	5	6	$\underline{59}$	8	1	0
S_5	0	0	2	9	$\underline{51}$	7	2
S_6	0	0	2	0	11	$\underline{50}$	10
S_7	1	0	0	0	1	8	$\underline{45}$

Results

The analysis of the pyridine concentrate B91 with the final matrix is given in Table VIII; the result obtained with a provisional matrix ($s_{ij} = 1$ for $i = j$ or 0 for $i \neq j$) — which eventually appeared to have been a reasonable approximation — is also given. The final matrix appears definitely more satisfactory in that it shows no "apparent" (5%) Q_{2n}-contents as does the provisional one; the actual quinolines content is negligible according to ultra-violet spectrometric analysis.

TABLE VIII

MASS-SPECTROMETRIC ANALYSIS OF PYRIDINE CONCENTRATE B91

		Final *%wt.*	*Provisional* *%wt.*
Py			
	0*n*	53	48
	1*n*	32	31
	2*n*	15	14
Q			
	0*n*	0	1
	1*n*	·3	1
	2*n*	.2	5
	3*n*	—	—

Further results with pyridine-quinoline concentrates obtained from petroleum distillate fractions are given in Fig. 2; underneath the detailed mass-spectrometric results the total pyridine and quinoline concentrations found by independent ultra-violet-spectrometric analysis are given in each case.

It is seen that indeed an important part of the basic fractions consists of various naphtheno-substituted compounds.

In a similar way certain *non-basic* nitrogen concentrates were found to consist predominantly (80+%) of carbazoles, including some 40% mono- and dinaphtheno-carbazoles (see Table IX).

TABLE IX

MASS-SPECTROMETRIC ANALYSIS OF A CARBAZOLE CONCENTRATE

Carbazoles	*%wt.*
alkyl-	34
mononaphtheno-	22
dinaphtheno-	15
total (MS)	~82
total (UV)	~80

BASIC NITROGEN–SULPHUR COMPOUNDS FROM PETROLEUM DISTILLATES

During the preparation of sulphur-free basic nitrogen concentrates, some fractions were found to contain both sulphur and nitrogen in the same molecule.

For the determination of these types of compounds a simple yet general approach as described in the first part of this paper is no longer possible. A combination of spectrometric and chemical techniques, however, was found very useful for unravelling the structure of such biheteroaromatic systems. The techniques employed may be summarized as follows:

1. Ultra-violet absorption spectra to judge the overall structure of the condensed heteroaromatic ring system.

2. Selective hydrogenation of the "pyridine part" of this system by means of tin and hydrochloric acid.

3. Mass spectra before and after the selective hydrogenation to ascertain the hydrogen uptake.

4. Ultra-violet spectra — after selective hydrogenation — in neutral and acidic solution to show among other things whether the basic nitrogen atom is attached directly to the remaining aromatic skeleton or separated from it by one or more nonaromatic carbon atoms.

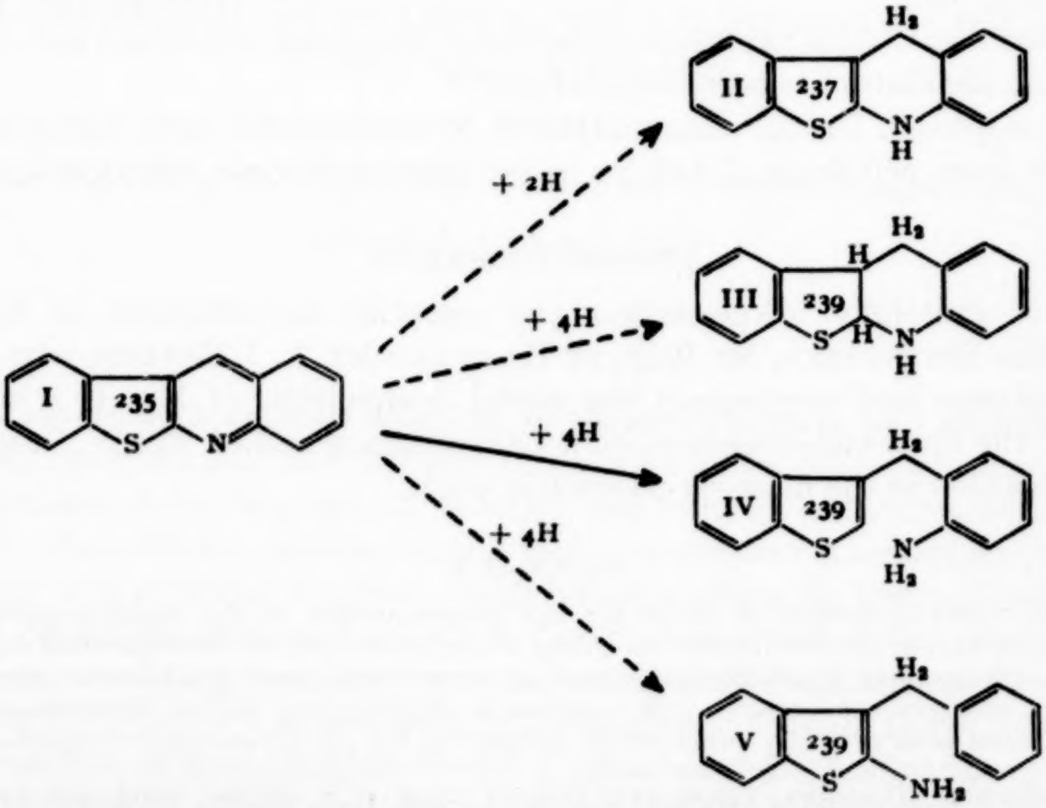


Fig. 3. Selective hydrogenation of 2,3-thionaphtho-2′,3′-quinoline.

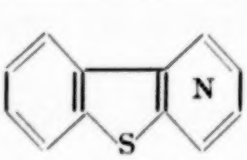
This procedure is perhaps best illustrated with a model compound of known structure, *viz.*: 2,3-thionaphtho-2′,3′-quinoline (mol.wt. 235); compound I of Fig. 3.

Upon selective reduction 4 H-atoms are taken up, as follows from the exclusive appearance of a parent peak at $m/e = 239$. This leaves III, IV and V as probable structures.

The ultra-violet spectra in neutral and acidic solution had a clearly composite character; they could be closely matched by superposition of an ortho-alkylaniline and an alkylthiophene spectrum in accordance with structure IV. The exceptional and unexpected ring opening giving the primary arylamino group was confirmed afterwards by other techniques.

Conversely, the evidence obtained ruled out the presence of a dibenzothiophene system in the original compound thus appreciably reducing the number of structures possible at the outset.

By means of this method the presence in actual concentrates of, among others, the following condensed biheteroaromatic ring systems could be demonstrated:



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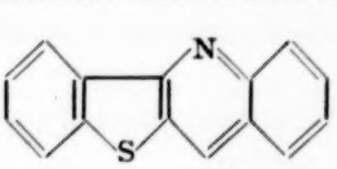

CONCLUSIONS

Mass-spectrometric analysis in proper combination with other techniques is capable of giving detailed information on the structure of heteroaromatic nitrogen compounds occurring in petroleum distillates.

Current concepts on total ionization have been verified for pyridines and quinolines having molecular weights of the order of 250. The data obtained were used in conjunction with other features to devise a matrix for the detailed analysis of pyridine–quinoline mixtures.

The presence of various naphtheno-substituted pyridines, quinolines and carbazoles in petroleum distillates has been demonstrated.*

A novel approach for the examination of heteroaromatic basic nitrogen-sulphur compounds from petroleum distillates is described and some results are presented.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the essential contributions of Dr. W. C. Brezesinska Smithuysen, Mr. W. F. de Haas and Mr. A. J. Mulder, who provided the concentrates and synthesized the model compounds, of Mr. J. Schout who performed the ultra-violet-spectrometric examinations and of Mr. W. G. van Wijk who collaborated in the mass-spectrometric work.

SUMMARY

A mass-spectrometric method is given for the determination of the pyridine-quinoline type distribution, including subdistribution according to naphthenicity, in corresponding concentrates from petroleum fractions. Its results are in good agreement with those of ultraviolet spectrometry. In non-basic nitrogen concentrates indole-carbazole distributions can be determined similarly. The method uses peak intensity summations comprising the parent and parent-minus-one series,

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* Independently, Dinneen, Cook and Jensen came to a similar conclusion for nitrogen compound types from shale oil–gas oil. (*Anal. Chem.* 30 (1958) 2026).

starting from the first naphtheno-aromatic skeleton conceivable that is built up of condensed five-membered naphtheno rings. It is based on current concepts on total ionization. The presence of mono- and dinaphtheno-pyridines, mono-naphtheno-quinolines and naphtheno-carbazoles in oil fractions was demonstrated. Besides, basic nitrogen concentrates were obtained containing one sulphur atom per heteroaromatic ring system. Here, combined application of mass- and ultraviolet spectrometry before and after selective hydrogenation led to detailed conclusions regarding their heteroaromatic nucleus.

RÉSUMÉ

L'auteur discute une méthode d'application de la spectrométrie de masse, pour déterminer, dans des fractions de pétrole concentrées, la distribution des composés du type pyridine-quinoléine, y compris leur distribution secondaire selon leur caractère naphténique. Les résultats correspondent bien avec ceux qu'on trouve en se servant de la spectrométrie dans l'ultraviolet. Il est également possible de déterminer de cette façon les distributions indole-carbazole dans des composés azotés concentrés non-basiques. La présence de pyridines mono- et dinaphténiques, de quinoléines mononaphténiques et de carbazoles naphténiques dans des fractions de pétrole a pu être démontrée.

ZUSAMMENFASSUNG

Zur Bestimmung der Verteilung der Verbindungen vom Typ Pyridin-Chinolin in konzentrierten Erdölfraktionen, einschlieszlich deren Verteilung nach naphtenischem Charakter, wurde eine massenspektrometrische Methode entwickelt. Die mit dieser Methode erzielten Ergebnisse weisen gute Übereinstimmung mit den mittels UV-Spektrometrie ermittelten auf. In ähnlicher Weise läszt sich auch die Indol-Karbazol-Verteilung in nichtbasischen Stickstoffkonzentraten bestimmen.

Er wurde nachgewiesen, dasz in Erdölfraktionen Mono- und Dinaphtenpyridine, Mononaphtenchinoline, Naphtenkarbazole sowie schwefelhaltige heteroaromatische Ringsysteme enthalten sind.

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THE COLORIMETRIC DETERMINATION OF DIALKYL PHOSPHITES USING CACOTHELINE

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Cacotheline reacts with aqueous solutions of various inorganic ions such as tin(II), titanium(III), uranium(III) and rhenium(III) to give a lilac colour which is due to a reduction product of the reagent[1], the reaction also being given by numerous organic compounds[2]. The stronger reducing agents such as stannous ion or sodium dithionite yield lilac coloured solutions, a colour change which is reversible, but continued action results in a colourless solution from which the original colour of the reagent is not regained. Some doubt has been cast upon the suitability of cacotheline for the estimation of tin(II)[3] whilst it has been noted that the system does not follow Beer's law[4]. The colour reaction of alkyl phosphites with 3,5-dinitrobenzoic acid has been used for the estimation of alkyl phosphites[5], this method involving a period of about one hour to develop the colour. Alkyl phosphites react with cacotheline in sodium carbonate solution to give an intense red solution the colour being formed immediately. A colorimetric method was required to deal with small quantities of alkyl phosphites and the use of the colour reaction with cacotheline for this purpose is described.

Experimental

The following dialkyl phosphites, available from laboratory preparations or supplied by Albright and Wilson Ltd., were examined: dimethyl, diethyl, di-isopropyl, di-*n*-butyl, and dibenzyl phosphite. All other materials used were of normal reagent grade. The spectra were recorded using a Hilger spectrophotometer with glass prism and 1-cm glass cells. This instrument was also used for the colorimetric estimations. The polarograms were recorded on Tinsley Recording Polarograph using a H-type cell one arm consisting of a saturated calomel electrode. All polarograms were recorded in media 0.1 M with respect to potassium chloride.

Results

The effect of increasing quantities of dimethyl phosphite upon the spectrum of cacotheline under the conditions used for the estimation is shown by Fig. 1. The red colouration produced in alkaline media is stable when the solution is made acid. The addition of dimethyl phosphite to a solution of cacotheline in pyridine resulted, after

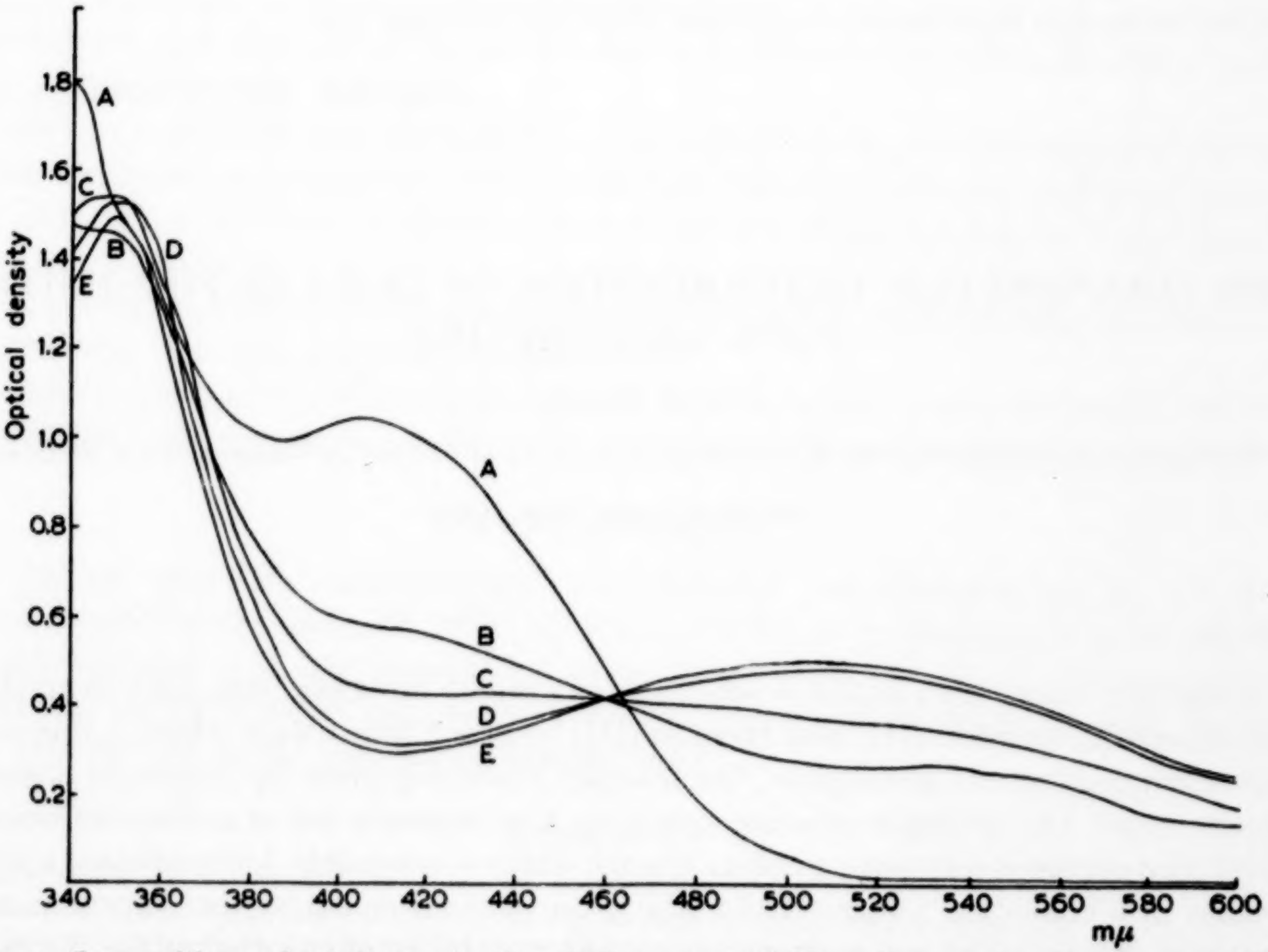

Fig. 1. Compositions of solutions: A. Cacotheline, $2 \cdot 10^{-4}\,M$; sodium carbonate, $0.5 \cdot 10^{-1}\,M$.
B. cacotheline $2 \cdot 10^{-4}\,M$; dimethyl phosphite, $2 \cdot 10^{-4}\,M$; sodium carbonate, $0.5 \cdot 10^{-1}\,M$.
C. cacotheline $2 \cdot 10^{-4}\,M$; dimethyl phosphite, $4 \cdot 10^{-4}\,M$; sodium carbonate, $0.5 \cdot 10^{-1}\,M$.
D. cacotheline $2 \cdot 10^{-4}\,M$; dimethyl phosphite, $6 \cdot 10^{-4}\,M$; sodium carbonate, $0.5 \cdot 10^{-1}\,M$.
E. cacotheline $2 \cdot 10^{-4}\,M$; dimethyl phosphite, $8 \cdot 10^{-4}\,M$; sodium carbonate, $0.5 \cdot 10^{-1}\,M$.

standing for a day, in the production of a green solution which eventually turned red. With the higher homologues some minutes were involved in colour production in aqueous sodium carbonate. The effect of dimethyl phosphite upon the polarographic response of cacotheline is shown by Fig. 2.

Other compounds containing the quinone group such as benzoquinone, chloranil, anthraquinone and alizarin showed no reaction with alkyl phosphites. Reagents which in alkaline solutions gave colour reactions with 3,5-dinitrobenzoic such as ethyl malonate, ethylacetoacetate and acetophenone gave no reaction with cacotheline. Monoalkyl phosphites give no colouration with cacotheline.

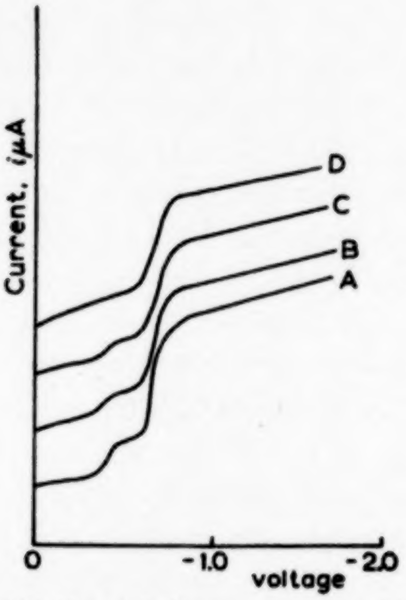

Fig. 2. Composition of solutions: All the solutions were 0.1 M in KCl and 0.1 M in Na_2CO_3. A. cacotheline $1 \cdot 10^{-4}$ M. B. cacotheline $1 \cdot 10^{-4}$ M; dimethyl phosphite $1 \cdot 10^{-4}$ M. C. cacotheline $1 \cdot 10^{-4}$ M; dimethyl phosphite $2 \cdot 10^{-4}$ M. D. cacotheline $1 \cdot 10^{-4}$ M; dimethyl phosphite $3 \cdot 10^{-4}$ M.

Procedure

5 ml of 1 N sodium carbonate were added to 5 ml of $2 \cdot 10^{-2}$ M cacotheline in a 50-ml flask. The sample of aqueous or ethanol solution of phosphite was then added and the solution made up to the mark. The cacotheline at this reagent strength shows some tendency to come out of solution on standing. By using 10 ml of $1 \cdot 10^{-2}$ M the reagent may be used for some time. The absorption of the solutions was measured at 560 mμ against the appropriate reagent blank using 1-cm cells. The choice of wavelength combined the required sensitivity with a reasonably low blank, and adherence to Beer's law. Typical calibration results are shown in Table I below for diethylphosphite.

TABLE I

Mg of diethylphosphite	*Absorption: 560 mμ*
0.2	0.015
0.5	0.059
1.0	0.117
1.5	0.187
2.0	0.248
2.5	0.301
3.0	0.360
4.0	0.490
5.0	0.602

The reagent blank at this wavelength had an absorption of 0.045 against water. Similar calibration curves were obtained for the other dialkyl phosphites. The absorption of the solutions was stable for at least three hours.

DISCUSSION

The spectra recorded indicate three moles of alkyl phosphite to one of cacotheline are required to develop the full colour. The reduction of cacotheline to its lilac product involves the addition of two hydrogen atoms to the reagent[6] and is the usual reduction product obtained. However a red colouration has been reported to be produced by the action of stannous chloride on the oxime of cacotheline[7].

The polarographic results confirm the spectrophotometric determinations in that the response at —0.40 V which is affected by the presence of dialkyl phosphite requires three times the molarity of cacotheline present before it is eliminated. By comparison with the collected data[8] this response is likely to be due to the quinone group whilst from the height and position the wave at —0.65 V to be due to the nitro-group which is not affected by the dialkyl phosphite. In the case of the interaction of dialkyl phosphites with 3,5-dinitrobenzoic acid in sodium bicarbonate media the polarograms show responses at —0.5 V and —0.65 V which are concerned with the reduction of the nitro groups. The heights of the waves are not affected by the presence of the dialkyl phosphite but instead a pronounced polarographic maximum the height of which is dependent on the concentration of dialkyl phosphite, occurs on the wave at —0.65 V.

SUMMARY

The estimation of dialkyl phosphites by means of its colour reaction with cacotheline in sodium carbonate solution is described. The effect of dialkyl phosphite upon the spectrum and polarographic response of the reagent is discussed to reveal the stoichiometry of the reaction and the group involved in colour production.

RÉSUMÉ

Les phosphites de dialcoyle donnent une réaction colorée avec la cacothéline, dans une solution de carbonate de sodium. Une étude spectrophotométrique et polarographique de cette réaction a été effectuée.

ZUSAMMENFASSUNG

Dialkyl-phosphite geben mit Kakothelin gefärbte Reaktionsprodukte, die sich zur spektrophotometrischen und polarographischen Bestimmung der Dialkyl-phosphite verwenden lassen.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

IV. A COMPARISON OF THE BAKER AND MORRISON CELL WITH THE RAlE.

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(Received July 27th, 1959)

In a previous paper[1] it was mentioned that BAKER AND MORRISON[2] introduced a simple cell for the rapid amperometric determination of traces of fluoride in solution. They used a straight piece of aluminum wire, 0.125 inch in diameter and 0.5 inch in exposed length as one electrode, and a 10 inch long and 0.03 inch diameter platinum spiral as the other electrode. The spontaneous current measured two min after short-circuiting the cell was found to be approximately proportional to the fluoride concentration in a solution 0.2 M in acetic acid or saturated with benzoic acid. It was stated that chloride causes serious interference at it yields a large current even in the absence of fluoride while in our recommended amperometric procedure[1] with the RAlE chloride does not interfere. It appeared of interest to compare the performance of the Baker and Morrison cell with that of the RAlE *vs.* the saturated calomel electrode (SCE) at an applied potential of —0.75 V and to investigate whether the interference by chloride (and other halides and also of perchlorate) in the Baker and Morrison cell cannot be eliminated by the choice of a simple reference electrode, the potential of which is considerably more negative than that of the platinum spiral in air-saturated solutions.

The solution in the Baker and Morrison cell is air-saturated, the platinum spiral being the positive electrode at which reduction of oxygen must occur when the cell

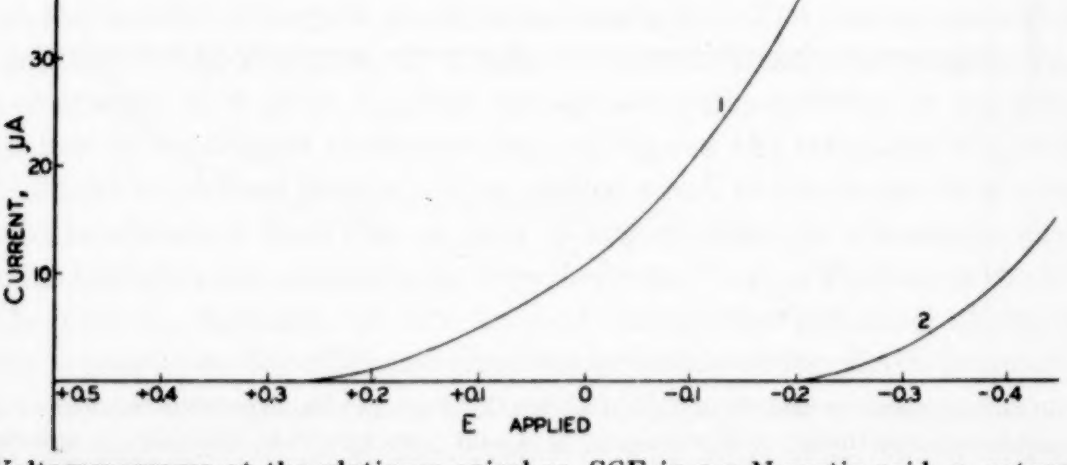

Fig. 1. Voltammograms at the platinum spiral *vs.* SCE in 0.2 N acetic acid. 1, saturated with air; 2, saturated with nitrogen.

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yields a spontaneous current in the presence of fluoride. In order to establish the potential of the spiral under conditions when current flows, we have determined current–potential curves at this electrode in air-saturated 0.2 *N* acetic acid *vs.* the SCE. The platinum spiral was of the same dimensions as that used by Baker and Morrison. A voltammogram is illustrated by curve a in Fig. 1. Upon passage of a current of 10 μA the potential was about 0 V *vs.* SCE. It became more negative with increasing current and was of the order of —0.2 V with a current of 35 μA. When such a platinum spiral is short-circuited against an aluminum electrode in an air-saturated 0.2 *N* acetic acid solution which contains some fluoride, the aluminum electrode nearly adopts the potential of the platinum electrode. In a previous publication[3] it was shown that chloride and the other halides and also perchlorate depolarize the aluminum electrode when its potential becomes less negative than about —0.6 V (*vs.* SCE). Thus these ions must interfere with the fluoride determination in the Baker and Morrison cell while they do not interfere at a potential of —0.75 V. Curve 2 in Fig. 1 gives a voltammogram in 0.2 *N* acetic acid in the absence of oxygen. When oxygen is removed from the Baker and Morrison cell, fluoride still produces a large current. Again the platinum spiral was found to be the positive electrode at which reduction of hydrogen ions occurs upon passages of current. When this current is small, the potential of the platinum electrode is of the order of 0.4 V more negative than in air-saturated solutions. At the potential in nitrogen the interference by chloride and perchlorate is considerably less than at a potential of about 0 V (*vs.* SCE)[3], but these ions still have some depolarizing effect on the aluminum electrode at a potential of about —0.4 V (*vs.* SCE).

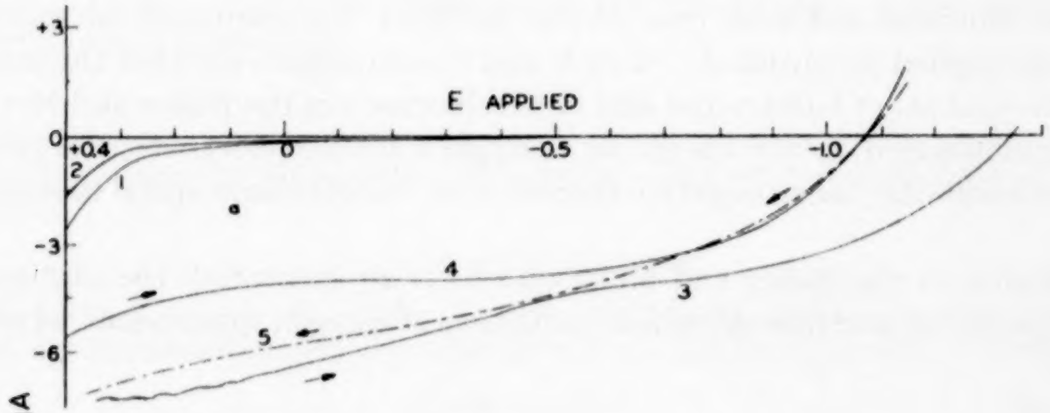

Fig. 2. Voltammograms in cell Pt 0.2 *N* HAc/RAlE. Fig. 2a: experimental curves; 1 and 2 no fluoride; 1, saturated with air; 2 in nitrogen; 3, 4 and 5 in $1 \cdot 10^{-4}$ *M* fluoride; 3, saturated with air; 4 and 5 in nitrogen. All run from + to — potentials except 5 in reverse direction (←). Fig. 2b: curves of Fig. 2a using the calculated potentials of RAlE *vs.* SCE as abscissa.

In order to substantiate the above conclusions several voltammograms were run in 0.2 *N* acetic acid using the RAlE *vs.* the platinum spiral as the electrode couple. As is to be expected hardly any current flows in the absence of fluoride over a wide range of potentials (from $+0.5$ to -1.5 V) as the two electrodes are highly polarized both in the presence and absence of oxygen (see Fig. 2a).

Curves 3, 4 and 5 are voltammograms of $1 \cdot 10^{-4}$ *M* fluoride in 0.2 *N* acetic acid in air (curve 3) and in nitrogen. The current in nitrogen is much better defined and smaller when run from positive to negative potentials (curve 4) than in the reverse direction. Qualitatively the same behavior was found in oxygen. Undoubtedly the reason is that the steady current value at a given potential cannot be registered by the polarograph when the applied potential is varied continuously with a reasonable speed. At a given potential the current, after rapidly attaining a large maximum value decreases to attain a steady value after about 40 sec in nitrogen and 70 sec in oxygen (see Fig. 3). The pattern of the curve of the residual current (in oxygen) is similar (curve 3, Fig. 3), but the current does not attain a steady value until after about 4 min.

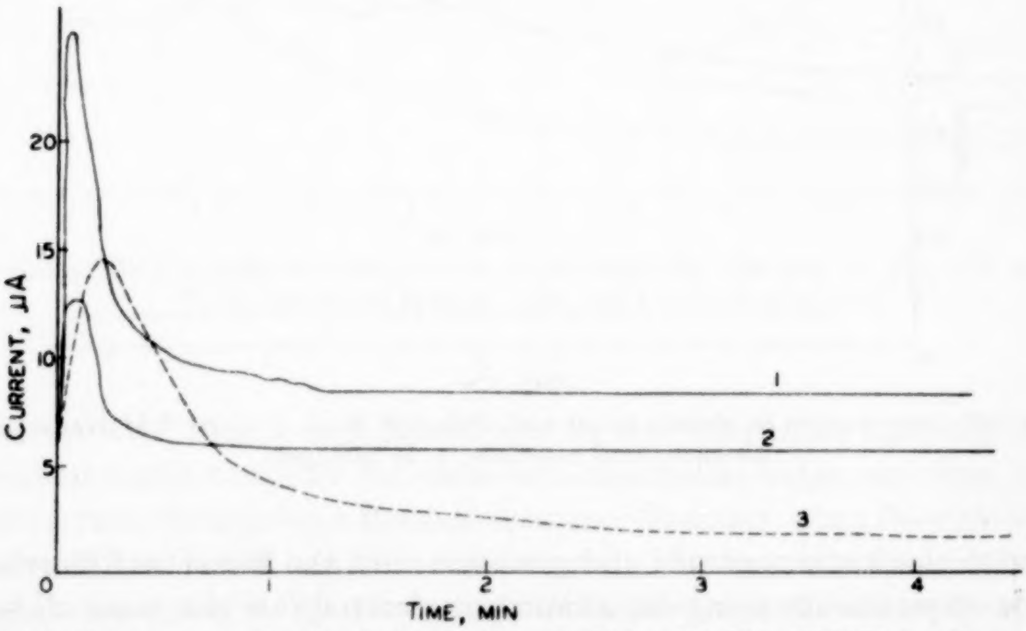

Fig. 3. Current–time curves in short-circuited cell Pt/0.2 *N* HAc/RAlE in the presence of $1 \cdot 10^{-4}$ *M* fluoride. 1, in air-saturated solution; 2, in nitrogen; 3 (dotted line) residual current in air (no fluoride).

In Fig. 2a the applied voltage is plotted on the abscissa. The current–potential curves plotted in oxygen and nitrogen can not be compared directly, because the potentials of both electrodes at a given applied voltage are quite different in oxygen than in nitrogen. For an intelligent understanding of Fig. 2a the potential of the RAlE *vs.* the SCE should be plotted instead of the applied e.m.f. If this is not done, the impression would be obtained from Fig. 2a that at zero current the aluminum electrode in air-saturated solutions is considerably more negative (-1.34 V) than in the absence of oxygen (-1.07 V). Actually, at zero applied voltage the potential of the platinum spiral was $+0.24$ V *vs.* the SCE and thus the potential of the RAlE becomes -1.1 V *vs.* SCE, while in nitrogen the potential of the platinum electrode was -0.24 V *vs.* SCE and the potential of the RAlE becomes -1.31 V *vs.* SCE. When current passes the potentials of the platinum electrode in oxygen and nitrogen become different from the zero-current potentials as is evident from Fig. 1. When (with the aid of data in Fig. 1) correction is made in Fig. 2a for the potential of the platinum electrode upon passage of current, curves are obtained as illustrated in Fig. 2b in which the abscissa now refers to the potential of the RAlE *vs.* SCE. As is to be expected, these curves are now very similar to voltammograms presented in previous publications.

When the cell was short-circuited ($E_{\text{applied}} = 0$ in Fig. 2a) the potential of the RAlE was —0.5 V (SCE) in oxygen and —0.41 V in nitrogen. As is to be expected from previous publications[1,3] the anodic depolarization of the RAlE by perchlorates and halides should be much greater at the potentials in oxygen than in nitrogen. This was actually observed and an example of such a depolarization by perchlorate is presented in Fig. 4.

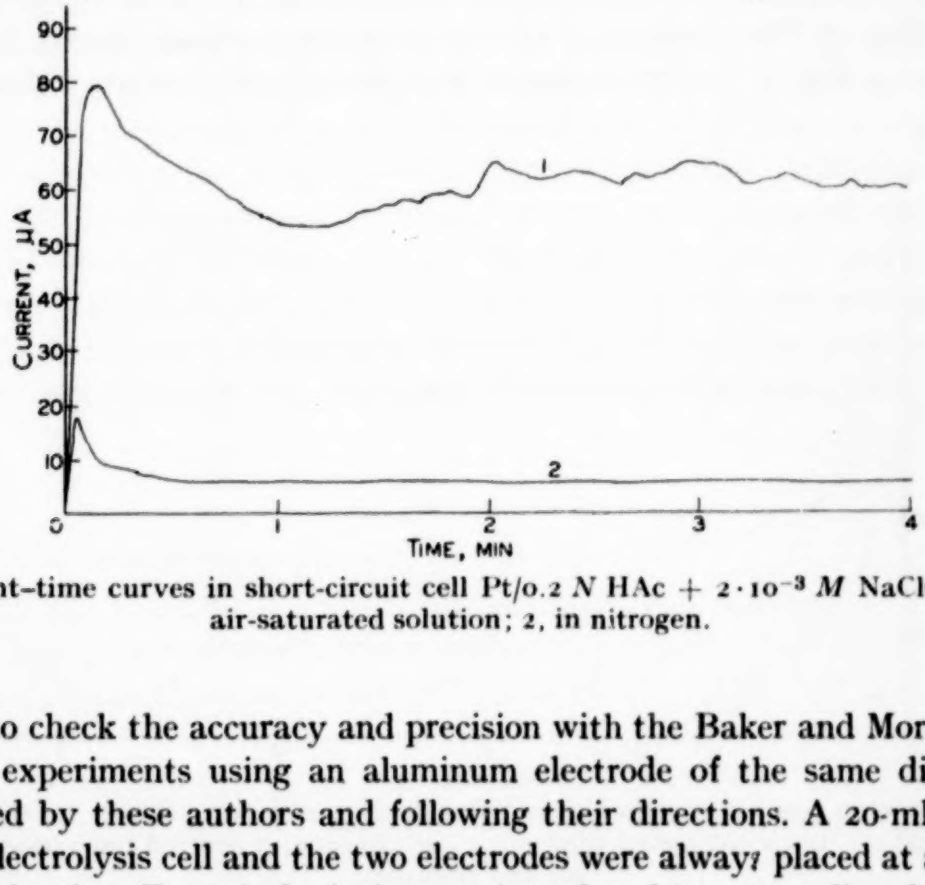

Fig. 4. Current–time curves in short-circuit cell Pt/0.2 N HAc + $2 \cdot 10^{-3}$ M $NaClO_4$/RAlE. 1, in air-saturated solution; 2, in nitrogen.

In order to check the accuracy and precision with the Baker and Morrison cell we have made experiments using an aluminum electrode of the same dimensions as recommended by these authors and following their directions. A 20-ml beaker was used as an electrolysis cell and the two electrodes were always placed at a distance of 2.6 cm of each other. Ten ml of solution was introduced into the cell and the contents stirred using a magnetic stirrer. Before each run the aluminum electrode was kept in 0.01 N hydrofluoric acid solution for 2 min. The reproducibility of residual currents and of fluoride currents in the measurement of current–time curves was found to be unsatisfactory in 0.2 N AcH. This could be attributed to a heating of the solution by the motor of the stirrer which became increasingly hot. Placing the beaker on a thick asbestos plate eliminated this interference. BAKER AND MORRISON[2] carried out most of their experiments in air-saturated 0.2 N acetic acid, but mention that a saturated benzoic acid solution is preferable when traces of fluoride (concentration of the order of 10^{-5} M) are to be determined. Indeed, we could confirm that the residual current is considerably smaller and better reproducible in saturated benzoic acid solution than in 0.2 N acetic acid. This is illustrated in Fig. 5.

After a short circuit of 2 min the current in 0.2 N acetic acid varied in 6 experiments between 15 and 22 μA after 2 min and between 8 and 14 μA after 5 min. In saturated benzoic acid solutions the current varied between 8.5 and 10 μA after 2 min and 4 and 6 μA after 5 min. **Baker and Morrison** measure the fluoride current after an electrolysis time of 2 min. Since this current must be corrected for the residual current a saturated benzoic acid solution would be preferable as a supporting electrolyte.

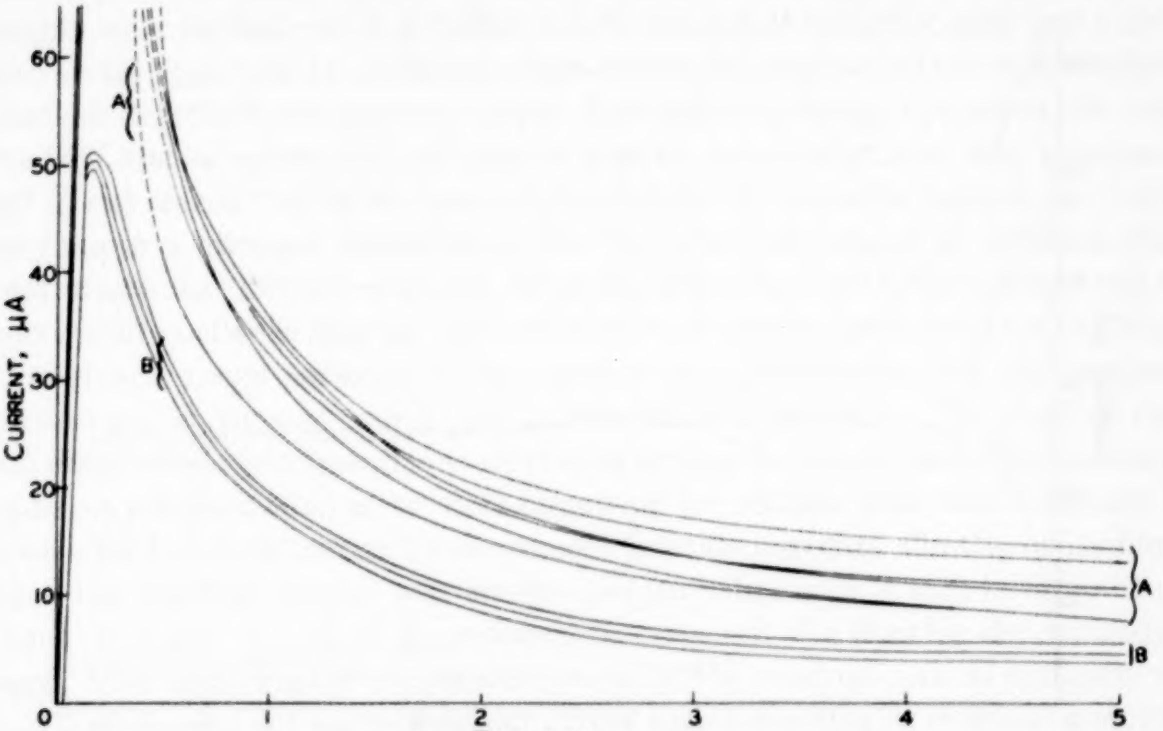

Fig. 5. Reproducibility of current–time curves of the residual currents. A, in 0.2 N acetic acid; B, in saturated benzoic acid; all air-saturated.

In agreement with **Baker and Morrison** we find that upon short-circuiting the cell the residual current rapidly increases to a maximum value and then decreases. The same pattern is observed in a fluoride solution. However, when fluoride was added to the solutions after the cell had been short-circuited for five minutes and the residual current had become practically constant, the fluoride current increased rapidly, but the current–time curve did not exhibit an acute maximum. The behavior is illustrated in Fig. 6. The above behavior must be considered in the construction of a calibration curve and in the determination of fluoride in an unknown.

The method of **Baker and Morrison** might find more general application if it were possible to eliminate the interference of some anions, particularly of chloride which yields a large current. The interference by halides and perchlorate in the Baker and Morrison method has been accounted for by the relatively large positive potential of the platinum electrode in an air-saturated solution. In our procedure with the RAlE the interference is eliminated by applying a potential of —0.75 V (*vs.* SCE). Using the Baker and Morrison method, but removing the oxygen with nitrogen, greatly improved the situation but did not eliminate the interference by chloride. This was to be expected since under these conditions the potential of the platinum electrode upon passage of spontaneous current was not negative enough to completely prevent depolarization of the aluminum electrode by chloride.

In the following experiments the supporting electrolyte was composed of 0.2 N acetic acid plus 0.02 M sodium acetate. From a practical point of view the use of a well-buffered solution is to be preferred over the slightly buffered 0.2 N acetic acid or a saturated benzoic acid solution in water. Using a prismatic rod of 99.9% pure lead, 1.25 cm long with an exposed surface of 0.8 cm^2 constant values of the residual current and of the fluoride current were attained after short-circuiting for 30 sec against the RAlE. Both in air-saturated solutions and in the absence of oxygen proportionality was found between fluoride concentration (in the range between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ M) and current. Whereas the potential of the platinum spiral in oxygen is considerably more positive than in nitrogen, the difference of the lead potential in both media is very small. Upon short-circuiting with the RAlE the lead potential was found to be —0.50 V in air-saturated solutions and —0.54 V (*vs.* SCE) in the absence of oxygen. About the same values were found both in the presence and absence of fluoride. The potential of the lead electrode is not negative enough to completely eliminate interference by chloride. After studying various other electrodes we finally selected a cadmium amalgam electrode, five percent in cadmium, in a suitable electrolyte. The following half-cells with 5% cadmium amalgam were prepared and their potentials (*vs.* SCE) measured at 25°: saturated with cadmium sulfate —0.605 V; 1 M in cadmium sulfate —0.632 V, 1 M in cadmium sulfate and saturated with potassium chloride —0.715 V; 1 M in cadmium sulfate and saturated with potassium bromide —0.770 V. As is to be expected these potentials are hardly altered upon passage of small currents. The last two electrodes should be suitable for our purpose, and we selected the half cell saturated with potassium chloride. The preparation of such a half cell is extremely simple and can be done quickly. A wide-mouthed bottle was used as the container and electrolytic contact made with the solution in the beaker containing either the RAlE or the Baker and Morrison electrode by means of a glass

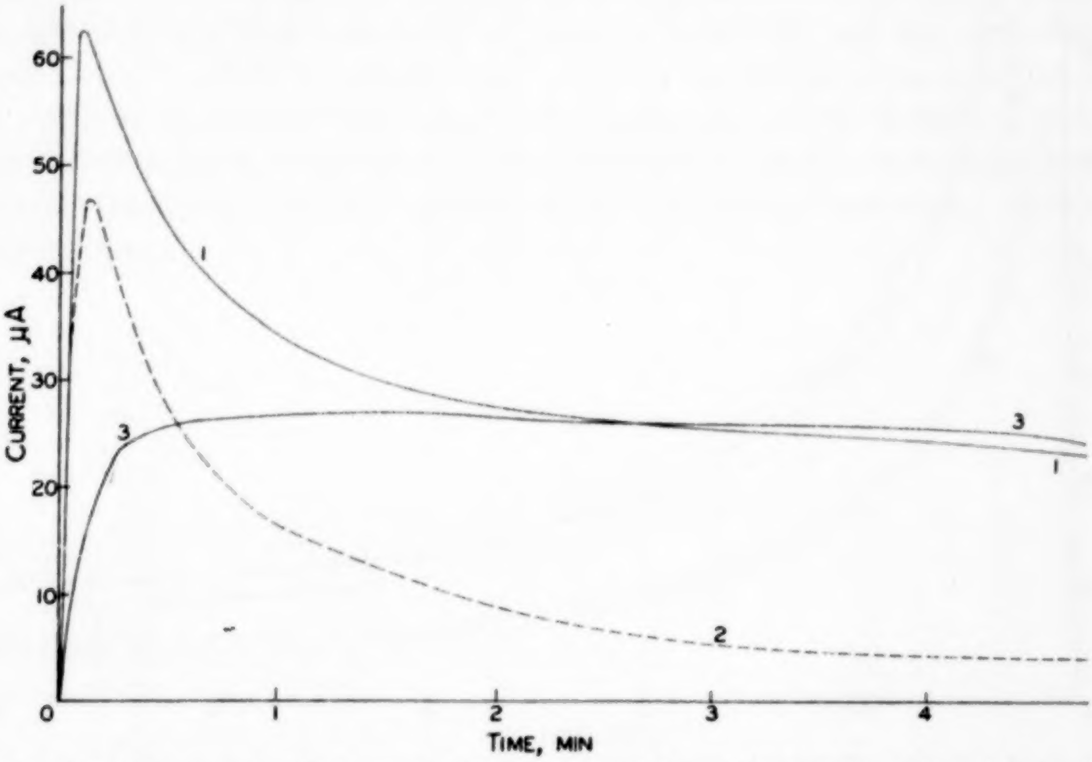

Fig. 6. Current-time curves (Baker and Morrison cell) in saturated benzoic acid. 1, clean electrode in $1.96 \cdot 10^{-5}$ M fluoride; 2, (dotted line) residual current (no fluoride); 3, $1.96 \cdot 10^{-5}$ M fluoride added after residual current had become constant.

U tube filled with a saturated potassium nitrate solution which was solidified with agar. Experiments with the RAlE were carried out with 50 ml solution, both in the presence and absence of oxygen. With the Baker and Morrison electrode we used a beaker of 20 ml, a volume of solution of 10 ml, while the solution was stirred with a magnetic stirrer (a thick asbestos plate prevented heating of the solution). All experiments were carried out in a buffer which was 0.2 *M* in acetic acid and 0.02 *M* in sodium acetate (pH 3.6). In a nitrogen atmosphere the response of the RAlE was found the same as described in a previous paper. Instead of applying a potential of —0.75 V *vs.* the SCE the cadmium half cell can be used in a short-circuited cell. In a previous paper[4] it was stated that in air-saturated solutions the fluoride current (at —0.75 V) is less than in a nitrogen atmosphere, but the effect of oxygen at different fluoride concentrations was not investigated. Studying this effect with the present cell linear proportionality between fluoride concentration and current (corrected for the residual) was found in a range between $1 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ *M* fluoride, but the proportionality constant in air was found 30% smaller than in nitrogen. The residual current (which varies somewhat from day to day) in air was 0.2 to 0.3 μA (cathodic) and changed to 0.4 to 0.5 μA (cathodic) after short circuiting for 10 min. This final constant value must be added as a correction to the anodic fluoride currents. On the other hand, in nitrogen the residual current was anodic and its value after 5 min became constant and equal to 0.3 to 0.4 μA. It is preferred to carry out the fluoride determination in nitrogen. After applying the proper correction for the residual current constant values of i/c of 0.56 ± 0.01 per micromole per l were found in nitrogen over a concentration range between $1 \cdot 10^{-5}$ and $2 \cdot 10^{-4}$ *M*. In air-saturated solutions i/c became equal to 0.42 ± 0.02 over the same concentration range. The lower fluoride current in the presence of oxygen has been attributed[1] to an electroreduction of oxygen at the RAlE in the presence of fluoride which results in a decrease of the anodic fluoride current. It is surprising and unexpected that i/c remains constant in the presence of oxygen. This must mean that at the RAlE the cathodic oxygen current increases in proportion to the concentration of fluoride present.

Using the standard addition method 0.01 *M* chloride or perchlorate were found not to interfere either in nitrogen or in oxygen. However, in the presence of 0.01 *M* chloride the residual current after 5 min (when it became constant) was 0.8 μA (cathodic) in air-saturated solutions, while it was 0.4 μA (cathodic) in the absence of chloride. In a nitrogen atmosphere the presence of 0.02 *M* chloride did not affect the residual current. In the presence of 0.005 *M* chloride in air-saturated solutions the same results were obtained as described above in the absence of chloride, provided proper correction for the residual current was made.

Using the Baker and Morrison electrode in a volume of 10 ml with magnetic stirring, the residual current in nitrogen was found constant after 1 min and equal to only 0.5 to 1.0 μA (anodic) and unaffected by the presence of 0.01 *M* chloride. In air-saturated solutions the residual current was cathodic and increased from 1.0 μA after one minute to 3–4 μA after 2 to 3 min. The presence of 0.01 *M* chloride did not affect these values; however, the automatically recorded current–time curves exhibited irregular oscillations of the current in the presence of chloride.

Fluoride currents remained reasonably constant when measured between 1.5 and 3.5 min after short-circuiting the cell. In nitrogen i/c was found constant and equal to 5.5 ± 0.2 (per micromole per l) over the concentration range between $1 \cdot 10^{-5}$ and

$1 \cdot 10^{-4}$ *M* fluoride. The concentration in an unknown can be estimated by the standard addition method[1].

In air-saturated solutions a large correction must be applied for the residual (cathodic) current and no satisfactory constant value of i/c was found. For example, the following values of i/c were observed: 4.5 in $1 \cdot 10^{-5}$ and $2 \cdot 10^{-5}$ *M* fluoride, 4.1 in $4 \cdot 10^{-5}$ *M*, 3.7 in $5.7 \cdot 10^{-4}$ an 2.9 in $7.4 \cdot 10^{-5}$ *M* fluoride.

In the presence of 0.0005 *M* chloride and in a nitrogen atmosphere the (anodic) residual current was 1 to 1.5 μA after 3 to 5 min and the value of i/c was the same as in the absence of chloride. In air-saturated solutions in the presence of 0.005 *M* chloride the residual current was the same as in the absence of chloride. However, periodic oscillations in the residual current and the fluoride current were observed. Again no linear proportionality between fluoride concentration and current was found. Thus the Baker and Morrison electrode short-circuited with the cadmium half cell is suitable for fluoride determinations when oxygen is removed from the solution. Using the RAlE removal of oxygen is recommended but not necessary.

In a previous paper[1] it was not stated that the RAlE, when not in use was kept in 0.01 *M* EDTA solution. When it was kept dry at the air the electrode became covered with a layer of oxide which could be removed by placing it in 0.01 *M* fluoride[2]. Similar observations were made with the Baker and Morrison electrode.

ACKNOWLEDGEMENT

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SUMMARY

In the amperometric determination of fluoride at the RAlE a half cell composed of 5% cadmium amalgam in equilibrum with a solution 1 *M* in cadmium sulfate and saturated with potassium chloride can be used as a reference electrode in a short-circuited cell instead of applying a potential of —0.75 V *versus* the saturated calomel electrode. The standard addition method can be used in the presence of air, although removal of oxygen is recommended. Using the Baker and Morrison electrode *versus* the above half cell and following their directions (10 ml solution, magnetic stirring) proportionality between current and fluoride concentration in a range between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ *M* was found in oxygen-free solutions. Halides and perchlorates do not interfere. The standard addition technique can be used in the determination of fluoride in an unknown.

RÉSUMÉ

Lors de leurs travaux sur l'emploi de l'électrode rotative en aluminium, en ampérométrie, les auteurs ont effectué une étude comparative entre cette dernière et l'électrode de BAKER ET MORRISON. Cette technique peut être utilisée pour le dosage des fluorures.

ZUSAMMENFASSUNG

An Hand von Studien über die Anwendung der rotierenden Aluminiumelektrode in der Amperometrie wird diese Elektrode im Vergleich mit der Elektrode von BAKER UND MORRISON betrachtet. Diese Methode eignet sich für die Bestimmung von Fluoriden.

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DETERMINATION OF SUBMICROGRAM QUANTITIES OF RUTHENIUM BY CATALYSIS OF THE CERIUM(IV)-ARSENIC(III) REACTION

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It has already been shown that amounts of osmium in the range 0.005–0.5 μg can be determined by the catalysis of the reaction

$$\mathrm{As(III)} + 2\ \mathrm{Ce(IV)} \rightarrow \mathrm{As(V)} + 2\ \mathrm{Ce(III)}$$

in sulfuric acid solution[1]. Even smaller amounts of ruthenium can be determined in the same way. The rate of the catalyzed reaction is conveniently determined spectrophotometrically by measuring the cerium(IV) concentration as a function of the time. A catalytic method is not likely to be of much value in practice unless the constituent being determined can be effectively separated from all the other constituents of the sample. The present paper, therefore, also deals with the separation of ruthenium as a necessary preliminary to the utilization of the method.

The catalytic method is intended for amounts of ruthenium that cannot be determined colorimetrically or by other methods (except such ultra-sensitive methods as neutron activation). There is no advantage in applying it when a colorimetric method can be used, since it is less convenient to carry out than the latter method. In general, the catalytic method will be of value for samples containing less than 1 p.p.m. Ru, or for larger relative amounts when the weight of sample available is limited.

Characteristics of the ruthenium-catalyzed reaction

The rate of the ruthenium-catalyzed ceric–arsenite reaction in 2.0 M sulfuric acid at 25.0° is given by the expression

$$-\frac{d[\mathrm{Ce(IV)}]}{dt} = \frac{4.0\cdot 10^{10}[\mathrm{Ru}]\,[\mathrm{Ce(IV)}]^{2.5}}{1 + 2.1\cdot 10^{3}[\mathrm{Ce(IV)}]^{1.5}}$$

where t is in minutes and concentrations are in moles/l². The rate is thus first order with respect to ruthenium but is a complex function of the cerium(IV) concentration*. The rate is independent of the arsenic(III), arsenic(V), and cerium(III) concentrations. Moreover, the sulfuric acid concentration in the range 0.5–2.0 M has little, if any, effect on the rate if the ionic strength is kept constant with sodium bisulfate. An increase in the ionic strength (addition of sodium perchlorate) increases the reaction rate slightly. Provided the ruthenium solution is first mixed with the ceric solution, it is immaterial whether ruthenium is originally present in the +4 or +8 oxidation state. If ruthenium (as RuO_4) is first added to the arsenite solution, the reaction rate is decreased and, moreover, depends on the manner of mixing the solutions[2]. The mechanism of the catalysis has not been elucidated.

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* In the osmium catalysis, the rate is determined by the arsenic(III), not the cerium(IV), concentration.

The preceding rate expression shows that the sensitivity of the catalytic ruthenium determination can be increased by increasing, within limits, the concentration of cerium(IV). Thus, with an initial Ce(IV) concentration of 0.04 N in the reaction mixture, the initial reaction rate is 5.5 times that with an initial Ce(IV) concentration of 0.01 N (Fig. 1). The optimum concentration is close to 0.04 N Ce(IV). A similar initial concentration of As(III) is suitable.

Determination of ruthenium in pure solution

In the absence of interfering substances, the determination of ruthenium is simply carried out by mixing the sample solution with ceric sulfate solution, allowing to stand for a few minutes if necessary to oxidize Ru(IV) to Ru(VIII), adding the mixture rapidly to arsenious oxide solution, and noting the time for the absorbance of the solution to decrease to some specified value. The absorbance is measured at a wave length that will allow the change in the concentration of cerium(IV) to be determined with adequate photometric precision. It is convenient to utilize a wave length at or near 488 mμ, which, under the conditions of the recommended procedure gives a transmittance of about 22% at zero time (1-cm cell). The time required for the transmittance to increase to 60% is noted. This interval, corresponding to the reduction of about 2/3 of the original amount of cerium(IV), is called the reaction time.

A plot of the reciprocal of the reaction time against the ruthenium concentration gives a straight line (Fig. 2). The equation for the ruthenium line in this figure is

$$\mathrm{Ru} = 0.0057(1/t - 0.0015),$$

where Ru is the concentration of ruthenium in p.p.m. (μg Ru per ml of solution) and t is in minutes. The value 0.0015 in this expression represents the correction to be made for the rate of the uncatalyzed reaction. In this particular case, the reaction time of the blank is about 670 min, corresponding to an apparent ruthenium concentration of $\sim 1 \cdot 10^{-5}$ μg Ru/ml. The blank reaction time sets the limit to the lowest concentration of ruthenium that can be detected or determined. With the blank mentioned, $1 \cdot 10^{-5}$ μg Ru/ml would be detectable and could be roughly determined. The limiting ruthenium concentration can then be set at 1 : 10^{11}. The blank reaction is in part due to a very slow uncatalyzed reaction between As(III) and Ce(IV) and in part to catalysis by impurities (iodine?). Although iodine, osmium and ruthenium are the only elements strongly catalyzing the ceric–arsenite reaction, it is conceivable that other elements or combinations of elements could have very weak catalytic activities, which might partly account for the blank reaction. Different batches of ceric sulfate have been found to give different blank reaction times, pointing to the presence of catalyzing impurities. The blank reaction time mentioned is not exceptional, *i.e.* some reagents have been found to give even slower reactions.

Under the conditions of the procedure, a convenient range of concentrations is from $5 \cdot 10^{-3}$ μg Ru/ml (reaction time a little longer than a minute) to $5 \cdot 10^{-4}$ μg Ru/ml (12 min). Reaction times other than the time corresponding to reduction of two-thirds of the cerium(IV) can, of course, be adopted and made the basis of a standard curve. Thus, in determining low concentrations of ruthenium, it may be more convenient to choose a reaction time corresponding to reduction of a smaller fraction of cerium(IV). Instead of measuring the time interval required for a given fraction of ceric sulfate to be reduced, the analyst can determine the amount which has been reduced at the end of some convenient fixed time interval such as 30 or 60 min. This procedure (which was not investigated in the present work) would be superior

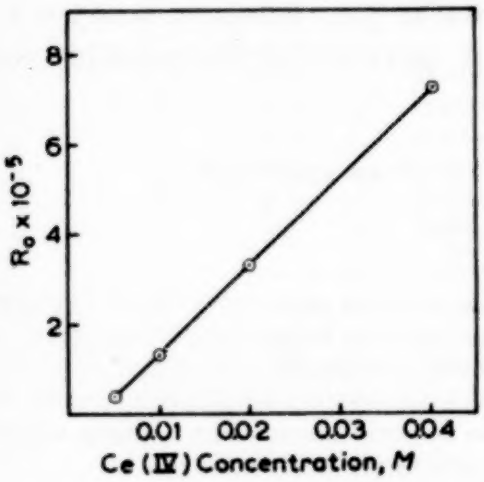

Fig. 1. Initial rate (R_0) of the ruthenium-catalyzed Ce(IV) – As(III) reaction as a function of the initial Ce(IV) concentration according to the rate equation in the text.

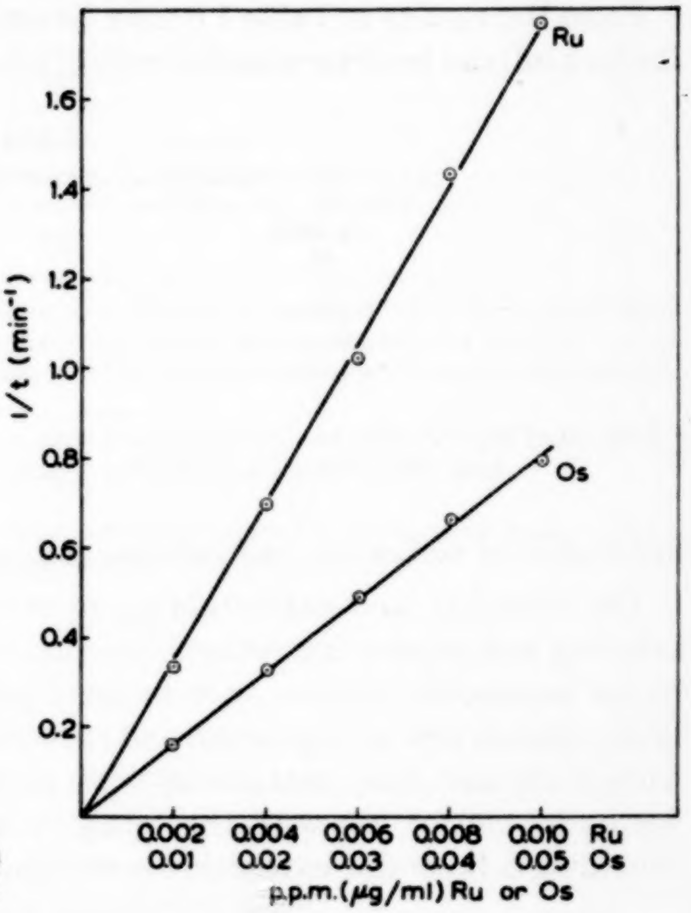

Fig. 2. Reciprocal of reaction time as a function of ruthenium and osmium concentration (25°).

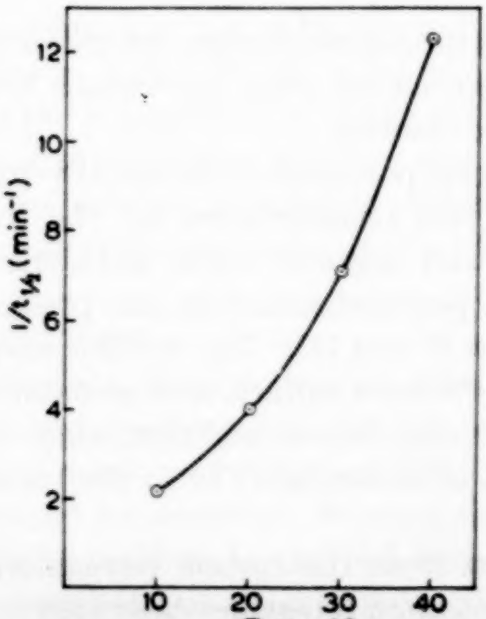

Fig. 3. Rate of ruthenium-catalyzed Ce(IV) – As(III) reaction as a function of the temperature. Rate is expressed as reciprocal of half-reaction time (0.02 N Ce(IV), 0.03 N As(III), 0.02 p.p.m. Ru).

for the lower ranges of ruthenium concentration. It would have the advantages of requiring less of the analyst's time and not requiring the use of a thermostated spectrophotometer; *i.e.*, the reaction mixture could be kept in a constant-temperature bath until shortly before the absorbance measurement. On the other hand, more work is needed to establish the standard curve, which is not linear.

As can be seen from Fig. 3, the temperature must be closely controlled in the catalytic determination. The reaction rate at 30° is 1.75 of that at 20°. A variation in temperature of 0.1° from 25.0° will cause an error of about 0.7%.

From the results in Table I it may be concluded that in pure solution, 0.005–0.1 μg Ru (in 2 ml) can be determined to within a few per cent, and 0.001 μg Ru to within 10%.

TABLE I

CATALYTIC DETERMINATION OF RUTHENIUM IN PURE SOLUTION[a]

Ru taken μg	*Ru found* μg		
0.0010	0.0011	0.0010	0.0010
0.0050	0.0049	0.0051	0.0049
0.0100	0.0098	0.0101	0.0098

[a] Two ml of Ru(IV) sulfate solution mixed with 1 ml of 0.160 *N* ceric ammonium sulfate solution and this solution added after 5 min to 1 ml of arsenious oxide solution.

Separation of ruthenium and subsequent determination

The volatility and extractability of ruthenium tetroxide offer the best means of isolating and separating ruthenium effectively from almost all elements. Extraction by an immiscible organic (non-oxygen) solvent is an attractive separation because final volumes can be kept small and ruthenium is obtained in an aqueous solution free from acids and other extraneous substances. Separation by extraction has therefore been adopted for use with the catalytic method. Carbon tetrachloride is a solvent providing a favorable extraction coefficient in neutral or acidic solutions[3]:

$$[\mathrm{RuO_4}]_{\mathrm{CCl_4}}/[\mathrm{RuO_4}]_{\mathrm{H_2O}} = 58.4 \quad (25^\circ)$$

The chief problems in the extraction separation are the oxidation of ruthenium to the +8 state, the transfer of ruthenium from the carbon tetrachloride to an aqueous phase, and the elimination of osmium.

Because of the high oxidation potential of the Ru(IV)–RuO$_4$ couple ($E_0 \sim -1.4$ V), few oxidizing agents come into consideration for the oxidation to the tetroxide. Potassium peroxydisulfate and argentic oxide were tried. Quantitative oxidation could not be obtained with peroxydisulfate in the presence of ferric salt. Argentic oxide proved suitable (Tables II and III). The solution may be 2 to 5 *M* in nitric acid or 0.5 to 2 *M* in sulfuric acid. When a sulfuric acid medium is used, it is best to dissolve the argentic oxide in nitric acid before addition, since it dissolves only slowly in sulfuric acid. The oxidation of ruthenium(IV) to the tetroxide is complete within 5 min at room temperature.

The transfer of ruthenium from the carbon tetrachloride extract to an aqueous phase is not as easy as with osmium tetroxide. Arsenious oxide solution, which is very suitable for osmium tetroxide, cannot be used because ruthenium is reduced to forms which do not have full catalytic activity. Sulfurous acid, as an acidified sodium sulfite

TABLE II

DETERMINATION OF RUTHENIUM AFTER SILVER(II) OXIDATION AND EXTRACTION WITH CARBON TETRACHLORIDE[a]

Concn. H_2SO_4 *M*	*Ru taken* *µg*	*Ru found* *µg*		
2	0.0010[b]	0.0010	0.0011	
2	0.0100[b]	0.0105	0.0090	
2	0.100[b]	0.099	0.098	0.101
0.5	0.100	0.097		
1.0	0.100	0.098		
2.0	—	0.00035		
2.0	0.0010	0.0012		
2.0	0.0050	0.0053		
2.0	0.010	0.0092	0.0094	
2.0	0.050	0.0495	0.0484	
2.0	0.100	0.096	0.099	(0.087)
3.0	0.100	0.095		

[a] Fifty ml Ru(IV) solution treated with silver(II) oxide dissolved in nitric acid, RuO_4 extracted with three 10-ml portions of carbon tetrachloride, the combined extracts shaken for 2 h with 10 ml of 0.005 *N* H_2SO_3 in 2 *M* sulfuric acid and Ru determined catalytically in the aqueous solution.
[b] Ru added as RuO_4 and oxidation step omitted.

TABLE III

DETERMINATION OF RUTHENIUM IN PRESENCE OF IRON AFTER SILVER(II) OXIDATION AND CARBON TETRACHLORIDE EXTRACTION[a]

Ru taken *µg*	*Ru found* *µg*		
—	0.00012		
0.00100	0.0012		
0.0100	0.0101	0.0100	
0.0500	0.0519	0.0508	
0.100	0.096	0.097	0.095

[a] 0.5 g iron as ferric sulfate in each determination.

solution, was found to be satisfactory for reducing and returning ruthenium to the aqueous phase, although slow in action. When 30 ml of carbon tetrachloride containing 0.10 µg of ruthenium as the tetroxide was shaken with 20 ml of 0.005 *N* sulfurous acid at 250 cycles per min, 83% of the ruthenium was transferred to the aqueous phase in the first 30 min. Two hours of mechanical shaking are needed for essentially complete transfer of ruthenium from the carbon tetrachloride to the aqueous phase.

Separation of ruthenium and osmium

The separation of these elements from each other is based on the difference in the ease of their oxidizability to the tetroxides. Two procedures were studied:

1. *Ferrous sulfate reduction–nitric acid oxidation:* This procedure has already been applied in the catalytic method for osmium[1]. When a slight excess of ferrous ion is added to a solution containing osmium in the +8 state and ruthenium wholly or partly in this state, ruthenium(VIII) is quickly reduced to lower oxidation states which are not converted to the tetroxide on subsequent addition of nitric acid to 5–6 *M* concentration, whereas osmium(VIII) is only slowly reduced, and the small

part that is reduced is restored to the tetroxide by the added nitric acid. Osmium tetroxide can then be extracted with carbon tetrachloride; ruthenium is left in the aqueous phase. The success of this method depends on the reduction of only a small fraction of the osmium(VIII), which means that the nitric acid must be added soon (within a few minutes) after the ferrous salt. If much osmium(VIII) is reduced, quantitative reoxidation is difficult, as shown elsewhere[4].

TABLE IV

DETERMINATION OF OSMIUM AND RUTHENIUM BY CATALYSIS AFTER SEPARATION BY $FeSO_4$–HNO_3–CCl_4 METHOD[a]

Ru taken µg	*Os taken* µg	*Ru found* µg	*Os found* µg
	0.100		0.095 0.093
	0.50		0.50
0.100	0.100	0.096	0.095
0.100	0.100	0.099	0.096
0.100	1.00	0.097	0.99

[a] Solution of Ru(IV) and Os(IV) in 35 ml of 2 *M* sulfuric acid treated with 0.1 *N* potassium permanganate to appearance of pink color, which was discharged with a slight excess of ferrous ammonium sulfate solution. Conc. nitric acid (15 ml) added and OsO_4 extracted with four 10-ml portions of carbon tetrachloride. Ruthenium extracted with three portions of carbon tetrachloride after Ag(II) nitrate oxidation.

The separation of osmium by extraction is especially advantageous when both osmium and ruthenium are to be determined (Table IV). The separation of osmium in this way becomes less easy when the ratio Os/Ru exceeds $\sim$ 100, because of the large number of extractions needed for the satisfactory removal of osmium. For example, if 50 ml of aqueous solution is extracted with four 10-ml portions of carbon tetrachloride, 99.6% of the osmium will be removed if the extraction coefficient is 15 (it is 14.8 in a solution of 1 *M* ionic strength). Accordingly, if the original amount of osmium is 100 µg, 0.4 µg will be left in the aqueous phase after the four extractions. Since, weight for weight, the catalytic activity of osmium is about 1/11 that of ruthenium under the recommended conditions for the determination of the latter (Fig. 2), this amount of residual osmium corresponds to about 0.04 µg Ru. With 1 µg Ru, the error due to osmium would then be +4%.

2. *Boiling with hydrogen peroxide:* When a sulfuric acid solution of osmium(IV or VIII) is boiled with hydrogen peroxide, osmium tetroxide is volatilized. Under the same conditions ruthenium(VIII) is reduced to the +3 or +4 state and is not volatilized[5]. The results in Table V indicate that osmium can be separated fairly satisfactorily from ruthenium in this way. Even at an Os/Ru ratio of 1000 (100 µg Os, 0.1 µg Ru), the error is within 10% on the average. There may be some compensation of errors, a little osmium apparently tending to remain in the aqueous phase.

As may be seen from Table V, the other platinum metals and much ferric iron and nickel do not interfere with the determination of ruthenium. Chloride can be removed by evaporating and fuming the sample with sulfuric acid. As much as 0.1 mg of iodine as iodide has no effect when separations are made as described.

Reagents

Arsenious oxide, 0.160 *N*: Dissolve 7.91 g of analytical reagent As_2O_3 in 25 ml of 1 *N* sodium hydroxide, dilute to about 200 ml with redistilled water, and add dilute sulfuric acid until acidic

TABLE V

DETERMINATION OF RUTHENIUM IN THE PRESENCE OF OSMIUM AND OTHER FOREIGN ELEMENTS[a]

Addition	*Ru taken* μg	*Ru found* μg		
—	0.0100	0.0095	0.0100	
—	0.100	0.098	0.100	
100 μg Os	—	0.006	0.004	0.003
100 μg Os	0.100	0.093	0.087	
[b]	—	0.0003		
[b]	0.005	0.006		
[b]	0.100	0.096	0.097	
10 μg Os[b]	0.005	0.006		
100 μg Os[b]	0.010	0.010	0.011	
100 μg Os[b]	0.100	0.087	0.093	
100 μg Os, 1 ml 6 *N* HCl[b]	0.100	0.096	0.097	0.090
100 μg I^- [b]	0.100	0.093	0.092	
100 μg Os, 100 μg I^- [b]	0.100	0.094		

[a] Ag_2O_2 oxidation and CCl_4 extraction of RuO_4 after removal of Os by boiling with hydrogen peroxide.

[b] 0.5 g Fe(III), 0.1 g Ni and 100 μg each of Pt, Pd, Rh and Ir present. Fumed with sulfuric acid.

to litmus paper. Then dilute to 1 l in a volumetric flask after adding enough sulfuric acid to make the final concentration 2.0 *M*.

Ceric ammonium sulfate, 0.16 *N* in 2.0 *M* sulfuric acid: Dissolve 101 g of the dihydrate in dilute sulfuric acid and dilute to 1 l. It is advisable to check the oxidizing normality of the solution by standardization against the arsenious oxide solution, with ferrous 1,10-phenanthroline complex as indicator and osmium tetroxide as catalyst, according to the usual procedure. A variation of a few per cent in strength from 0.160 *N* is of no importance. The solution should preferably be allowed to stand for a week and any precipitate filtered off before standardizing.

Standard ruthenium solution: Prepare a stock solution of ruthenium(III or IV) sulfate of convenient strength, *e.g.* 1 to 2 mg Ru per ml, in 2 *M* sulfuric acid (*cf.* Note 1). Standardize by precipitating hydrous ruthenium oxide at pH 6 with sodium bicarbonate and igniting to ruthenium metal in hydrogen according to the usual procedure. Dilute the stock ruthenium solution stepwise with 2 *M* sulfuric acid to obtain solutions of convenient ruthenium concentration, *e.g.* 0.01 μg Ru/ml.

Carbon tetrachloride: Shake a reagent quality product with 0.1 *N* potassium permanganate for several hours. Separate the phases and shake the carbon tetrachloride with several portions of concentrated sulfuric acid and wash with water. Saturate the carbon tetrachloride with chlorine and reflux for a few hours. Remove chlorine by shaking with several portions of 2 *M* potassium hydroxide. Wash the carbon tetrachloride with water until neutral to litmus paper, dry with anhydrone, and distil. Store in the dark.

Silver(II) oxide: This can be obtained by adding a solution of potassium peroxydisulfate, which has been made strongly basic with potassium hydroxide, to a boiling solution of silver nitrate, boiling until oxygen evolution ceases, filtering and washing the precipitate with hot water[6].

Procedure

The sample solution may conveniently contain 0.005–0.1 μg Ru. If halides are present add 5 ml of 1 : 1 sulfuric acid, evaporate to fumes, and continue fuming lightly to moderately for 30–60 min. Especially if much solid separates, it is well to take up the residue in water after fuming for one-half hour and again evaporate and fume to assure elimination of halides. Strong oxidizing agents such as nitric acid which could lead to loss of ruthenium tetroxide must be destroyed, as by evaporation with conc. hydrochloric acid. If osmium is to be determined simultaneously, ferrous sulfate must be added to prevent loss of osmium tetroxide on fuming.

Separation of osmium. If the weight ratio Os/Ru does not exceed 50–100, proceed according to (a), otherwise, in general, by (b):

(a) Carbon tetrachloride extraction of osmium tetroxide. Make the sample solution approximately 2 *M* in sulfuric acid. If the solution was evaporated to fuming, dilute to roughly this acidity. The final volume of the solution should not be greater than about 40 ml for the volume of carbon tetrachloride specified below.

To the cold solution add 0.1 *N* (or stronger if necessary) potassium permanganate with mixing until the solution just becomes pink. After 2 or 3 min destroy the excess permanganate by adding 50 mg of ferrous ammonium sulfate hexahydrate dissolved in a milliliter or two of water and mix well. Within a minute or two add 15 ml of conc. nitric acid (or more as necessary to make its concentration 5 to 6 *M*).

Extract osmium tetroxide from the cold solution with four 10-ml portions of carbon tetrachloride, shaking vigorously for one-half minute each time. Discard the carbon tetrachloride extracts unless osmium is to be determined also[1].

(b) Elimination of osmium by boiling with hydrogen peroxide. Dilute the fumed solution to 100 ml with water (0.5–1 *M* in sulfuric acid). Add a few drops of 30% hydrogen peroxide or more (1–2 ml) if ferrous iron is present. Boil in a beaker, with protection against mechanical loss, until the volume is reduced to one-half. Repeat the evaporation twice after restoring the volume with water and adding more hydrogen peroxide.

Oxidation and extraction of ruthenium. Add 0.5 g argentic oxide to the cold solution from which osmium has been removed and stir to dissolve. (In the absence of nitric acid — removal of osmium tetroxide by boiling — dissolve the argentic oxide in a little 5 *M* nitric acid and add this to the solution). Allow to stand 10 min at room temperature. Extract ruthenium tetroxide with three 10-ml portions of carbon tetrachloride. Shake the combined carbon tetrachloride extracts with 5 ml of 2 *M* sulfuric acid containing a little argentic oxide and discard the aqueous phase. The phases must be carefully separated.

Shake the carbon tetrachloride extract in a mechanical shaker for 2 h with 10.0 ml of 2.0 *M* sulfuric acid to which 3.2 mg of Na_2SO_3 has been added. If necessary clarify the aqueous layer by centrifuging, separate the phases, and discard the carbon tetrachloride.

Determination of ruthenium. Bring the aqueous solution to 25.0° and introduce a 2.00-ml aliquot and 1 ml of ceric ammonium sulfate solution into a hypodermic syringe (see Note 3). Thermostat the loaded syringe for 10 min. Then inject the solution as rapidly as possible into 1.00 ml of arsenious oxide solution (25.0°) in a 20-ml beaker. Start a stop watch or chart driving motor simultaneously with the mixing. Transfer the solution to a dry 1-cm cell, thermostated at 25.0°, and obtain the time required for a transmittance of 60% (against water) to be reached at 488 mμ (Note 4).

Establish the standard curve by taking 2.00-ml portions of Ru(III or IV) sulfate (0.001–0.02 μg Ru) in 2 *M* sulfuric acid and proceeding as above. Plot the reciprocal of the reaction time against the ruthenium concentration.

Notes: 1. It may be possible to prepare ruthenium sulfate by long-continued fuming of ruthenium chloride or ammonium chlororuthenate with sulfuric acid. The last traces of chloride are difficult to expel however.

2. A standard ruthenium(IV) sulfate solution in 2 *M* sulfuric acid containing 0.01 μg Ru per ml has been found to show no apparent change in concentration in a year's time.

3. Instead of a syringe, a small beaker can be used, with addition of the sample and

ceric mixture at one stroke to the arsenic solution, followed by return of the mixture to the first beaker and then to the absorption cell.

4. The transmittance of a mixture of 1 ml each of ceric ammonium sulfate and arsenious oxide solutions and 2 ml of water should be approximately 22%.

5. When the concentration of ruthenium is low, it may be advantageous to measure the reaction rate by finding the amount of cerium(IV) reduced in a fixed time interval, as mentioned in the text.

SUMMARY

Ruthenium in amounts of 0.005–0.1 μg (and less if need be) can be determined by its catalysis of the slow reaction between cerium(IV) and arsenic(III) in sulfuric acid solution. The rate of the catalyzed reaction is obtained by measuring the concentration of cerium(IV) spectrophotometrically as a function of the time. Ruthenium is first separated by carbon tetrachloride extraction of the tetroxide, following argentic oxide oxidation. Osmium tetroxide is removed by prior extraction with carbon tetrachloride after differential oxidation with nitric acid. Osmium can also be removed by boiling an acid solution with hydrogen peroxide, ruthenium being left in solution.

RÉSUMÉ

Il est possible de doser des teneurs en ruthénium de 0.005–0.1 μg grâce à son action catalysante sur la réaction lente entre le cérium(IV) et l'arsenic(III), en solution sulfurique. On effectue la détermination en mesurant spectrophotométriquement les variations de la concentration en cérium(IV) en fonction du temps. Le ruthénium est séparé au préalable par extraction au moyen de tétrachlorure de carbone après oxydation en tétroxyde par l'oxyde d'argent(II).

ZUSAMMENFASSUNG

Spuren von Ruthenium (0.005–0.1 μg) können durch seine katalytische Wirkung auf die langsame Reaktion zwischen Cer(IV) und Arsen(III) in schwefelsaurer Lösung bestimmt werden wobei die Änderung der Cer(IV)-Konzentration in Abhängigkeit von der Zeit spektrophotometrisch verfolgt wird. Die Abtrennung des Rutheniums vom Osmium erfolgt durch Lösungsmittelextraktion nach dessen Oxydation mit Silber(II)-oxyd.

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REACTIONS BETWEEN ALKALOIDS AND BISMUTH IODIDE, THE COMPOUNDS FORMED AND THEIR ANALYTICAL APPLICATION

A HETEROMETRIC STUDY*

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INTRODUCTION

The reaction between pyramidon and bismuth iodide was studied by us heterometrically[1]. More than *ten* well defined stoechiometric compounds were obtained. Each of four of them could be used for a precise determination of either bismuth or pyramidon. The composition of these latter final compounds (= ↓↓) depended on which of the three components (iodide, bismuth nitrate, or pyramidon) was used as titrant.

We were interested to study other complicated cyclic N-compounds on a similar basis. This investigation had a double purpose. Firstly, to study the reactions with the individual N-compounds, so as to establish the *final* as well as the *intermediate* compounds obtained. We hoped in this way to obtain a deeper insight into the function of each nitrogen atom built into the organic molecule. In many cases, the type of final compound obtained depended on the stereochemistry of the compounds. Although our main attention was directed to the alkaloids, other specific N-compounds, such as phenanthroline, nitron, pyramidon, etc. were also included for comparison. Secondly, we were interested to investigate the analytical application of the reactions for a rapid and precise determination of alkaloids or other complex N-compounds. The next step may be the determination of individual N-compounds in mixtures.

The results presented here seem to justify our interest from both aspects, the general chemical and the analytical, which are very closely connected in heterometry.

EXPERIMENTAL

Reagents

The following reagents were used.

Bismuth nitrate. $Bi(NO_3)_3 \cdot 5H_2O$, Baker's 'Analyzed'. A 0.05 *M* solution in 1 *N* nitric acid was prepared. More dilute solutions were prepared from the stock solution by diluting with acidified water, so that in the final solutions the molar concentration of nitric acid was approximately 22 times that of bismuth.

Potassium iodide. Baker's 'Analyzed'. A 0.5 *N* aqueous stock solution was prepared. More dilute solutions were freshly prepared and kept in dark brown bottles.

Nitron. Eastman Organic Chemicals, for chemical purposes. 0.7802 g nitron + 7 ml *N* CH_3-COOH were dissolved in water and made up to 250 ml giving a 0.01 *M* solution. More dilute solutions were prepared from the standard solution. All solutions were kept in dark brown bottles. The dilute solutions were freshly prepared every few days.

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* Dedicated to Prof. WALTER FEITKNECHT, Bern, on his 60th birthday.

Quinine. $C_{20}H_{24}N_2O_2 \cdot HCl \cdot 2H_2O$ (Pharmacie Centrale de Belgique SA. Bruxelles, M.W. 396.9. 0.3969 g were dissolved in 100 ml water (0.01 M).

Cinchonine. Fisher Scientific Company, $C_{19}H_{22}N_2O$. M.W. 294.58, 0.2946 g were dissolved in 100 ml 0.02 M HNO_3 (0.01 M).

Strychnine sulphate. (neutral I). Boehringer und Soehne. M.W. 856.97, B.P.C. 49, 0.4285 g in 100 ml water (0.01 M).

Sparteine sulphate. $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$, M.W. 422.5, 0.4225 g in 100 ml water (0.01 M).

Papaverine hydrochloride. Roche DAB, $C_{20}H_{21}NO_4 \cdot HCl$, M.W. 375.8, 0.3758 g in 100 ml water (0.01 M).

Rivanol. Bubeck & Dolder ex. S. H. Wolfensberger & Co. (lactate). $C_{15}H_{15}ON_3 \cdot C_3H_6O_3 \cdot H_2O$, M.W. 361.3, 0.3613 g in 100 ml water (0.01 M).

Acriflavine. I.C.I. $C_{14}H_{14}N_3Cl \cdot HCl$, M.W. 296.2, 0.2962 g in 100 ml water (0.01 M).

1 : 10 Phenanthroline. B.D.H., AnalaR. $C_{12}H_8N_2 \cdot H_2O$, M.W. 198.22, 0.1982 g in 100 ml water (0.01 M).

Atropine sulphate. May & Baker, $(C_{17}H_{23}O_3N)_2 \cdot H_2SO_4 \cdot H_2O$, M.W. 694.80, 0.6948 g in 100 ml water (0.02 M).

Antipyrine. B.P. May & Baker, $C_{11}H_{12}ON_2$, M.W. 188.22. 0.1882 g in 100 ml water (0.01 M).

Pyramidon. Bubeck & Dolder Ph. H.V., $C_{13}H_{17}ON_3$, M.W. 231.29, 0.2313 g in 100 ml water (0.01 M).

Method

The same instruments and the same working conditions were used as in previous heterometric investigations[2]. The fundamental principles of heterometry have been presented before[3]. The temperature was always 20°.

RESULTS AND DISCUSSION

General

A selection of experiments carried out, and the results obtained, are presented in tables and figures. Each of the Tables I–III presents experiments using a different titrant. The course of some experiments are also presented in figures which correspond to the tables (the same numeration is used in both cases). In the Figs. 1–3 are cited the molar ratios of [Bi] : [titrant] found at the critical points of the formation of the intermediate and the final compounds.

A glance at the curves shows that in most curves many critical points were established corresponding to definite compounds formed stoechiometrically. In most cases the end-points exactly coincided with the first maximum density point (= ↓↓), after which a horizontal maximum density line was obtained. Thus each curve presented a series of *intermediate* compounds terminating with a *final* compound. The sequence of compounds, their character and composition depended on the titrant used. Analysing the results of Tables I, IV and V we can classify the different N-compounds and can define the role of each nitrogen atom in the complicated organic molecules. The reactions and the compounds obtained were largely dependent on the stereochemical character of the individual N-compounds participating in the formation of the insoluble compounds.

Table I shows that the *first* maximum density point could almost always be used for the determination of the N-compound. A full titration took 10–15 min and the error was usually negligible. The sensitivity of the reaction towards different alkaloids varied. In most cases (Table V) 0.5 to 1.0 mg of alkaloid was sufficient for an analysis. The titration time of 10–15 min was somewhat extended because all the intermediate critical points were considered. For analytical purposes the first maximum point only has to be considered. This may probably rather shorten the titration time.

TABLE I

General composition: *a* ml *k* *M* nitrogen compound (= A) + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KJ + ad 10 (or ad 20) water + *x* ml *m* *M* $Bi(NO_3)_3$. T = 20°.
Filter: red.

Expt. No.	*Solution of nitrogen compound*		*$Bi(NO_3)_3$*			*% error*	*Optical density at the end-point*	*Molar ratio [Bi] : [A] at end-point*	*Titration time in min*	*Remarks*
			Molarity	*ml calculated*	*ml found*					
1	5 ml 0.002 *M* Nitron (+ 1 ml *M* HNO_3)	+ 12 ml H_2O								Precipitation before the beginning of titration.
2	3 ml 0.001 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 14 ml H_2O	0.002				>1.0			Sulfuric instead of nitric acid.
3	3 ml 0.0005 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 14 ml H_2O	0.001	3.00	i 3.00 h	0.0	0.94	2 : 1	12	
4	3 ml 0.00025 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 14 ml H_2O	0.0005				0.30			No definite end-point; low density
5	3 ml 0.0005 *M* Nitron (+ 1 ml 0.5 *M* H_2SO_4)	+ 16 ml H_2O	0.001		>5.0		0.0			Blank: *without* KJ.
6	3 ml 0.0005 *M* Quinine	+ 14 ml H_2O	0.00083	3.60	i 3.60 h	0.0	0.81	2 : 1	14	
7	3 ml 0.001 *M* Cinchonine	+ 14 ml H_2O	0.00167				>1.0			Too high optical densities.
8	3 ml 0.0005 *M* Cinchonine	+ 14 ml H_2O	0.001	3.00	i 3.00 h	0.0	0.67	2 : 1	14	
9	4 ml 0.001 *M* Strychnine	+ 3 ml H_2O	0.00167	2.40	2.40 h	0.0	0.81	1 : 1	12	
10	4 ml 0.001 *M* Strychnine	+ 3 ml H_2O	0.0013	3.20	i 3.20 h	0.0	0.88	1 : 1	14	
11	8 ml 0.0003 *M* Sparteine	+ 9 ml H_2O	0.00167	2.88	i 2.90 h	0.6	0.91	2 : 1	12	
12	5 ml 0.0005 *M* Papaverine	+ 2 ml H_2O	0.001	2.50	i 2.50 h	0.0	0.67	1 : 1	10	
13	4 ml 0.00167 *M* Rivanol	+ 3 ml H_2O								Precipitation before the beginning of titration.
14	4 ml 0.00167 *M* Rivanol	+ 13 ml H_2O								
15	3 ml 0.001 *M* Rivanol	+ 14 ml H_2O	0.001	3.00	i 2.99 h	0.3	0.84	1 : 1	12	
16	4 ml 0.000833 *M* Rivanol	+ 13 ml H_2O	0.00167	2.00	2.00	0.0	0.72	1 : 1	10	
17	3 ml 0.001 *M* Acriflavine	+ 4 ml H_2O	0.001	3.00	i 3.00 h	0.0	0.64	1 : 1	15	
18	5 ml 0.001 *M* Phenanthroline	+ 2 ml H_2O	0.00167	3.00	i 3.00 h	0.0	0.84	1 : 1	12	
19	4 ml 0.0013 *M* Antipyrine	+ 3 ml H_2O	0.0033	3.00	i 3.00 h	0.0	0.68	2 : 1	12	
20	3 ml 0.002 *M* Atropine	+ 4 ml H_2O	0.00167	3.60	i 3.60 h	0.0	0.73	1 : 1	10	

i = intersection point; h = horizontal maximum density line.

TABLE II

General composition: *a* ml *k* *M* $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KJ + ad 10 (or ad 20) water + *x* ml *m* *M* nitrogen compound. T = 20°.
Filter: red.

Expt. No.	Solution of bismuth nitrate	Titrated vol. ml	Nitrogen compound							Titration time in min	% error	Remarks
			Name	Molarity	ml calculated	ml found	Max. optical density	Ratio [Bi] : [A]				
1	6 ml 0.0005 *M* $Bi(NO_3)_3$	20	Quinine	0.0005	3.00	i 3.00 h	0.89	2 : 1		14	0.0	
2	3 ml 0.001 *M* $Bi(NO_3)_3$	10	Papaverine	0.001	3.00	i 3.00 h	0.77	1 : 1		12	0.0	
3	3 ml 0.001 *M* $Bi(NO_3)_3$	10	Acriflavine	0.001	3.00	i 3.00 h	0.72	1 : 1		14	0.0	
4	1 ml 0.5 *M* H_2SO_4 + (5 ml 0.02 *M* HNO_3)	20	Nitron	0.0005		>5.0	0.0					Blank, no precipitation.
5	3 ml 0.001 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	20	Nitron	0.001	3.00	i 3.00 h	0.96	1 : 1		12	0.0	
6	3 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	20	Nitron	0.0005	3.00	i 3.00 h	0.69	1 : 1		14	0.0	
7	3 ml 0.001 *M* $Bi(NO_3)_3$	20	Cinchonine	0.0005	3.00	i 2.97 h	0.55	2 : 1		14	1.0	
8	4 ml 0.00167 *M* $Bi(NO_3)_3$	10	Rivanol	0.002								No definite end-point.
9	3 ml 0.001 *M* $Bi(NO_3)_3$	20	Rivanol	0.001	3.00	i 3.00 h	0.47	1 : 1		14	0.0	
10	4 ml 0.001 *M* $Bi(NO_3)_3$	10	Strychnine	0.001	4.00	i 4.00 h	0.96	1 : 1		12	0.0	
11	5 ml 0.001 *M* $Bi(NO_3)_3$	10	Phenanthroline	0.00167	3.00	i 3.00 h	0.85	1 : 1		12	0.0	
12	3 ml 0.00167 *M* $Bi(NO_3)_3$	10	Antipyrine	0.00133	4.00	i 4.00 h	0.51	1 : 1		15	0.0	
13	4 ml 0.00133 *M* $Bi(NO_3)_3$	20	Sparteine	0.00167								Too high optical densities.
14	4 ml 0.0005 *M* $Bi(NO_3)_3$	20	Sparteine	0.00083								Too low optical densities.
15	5 ml 0.001 *M* $Bi(NO_3)_3$	20	Sparteine	0.00083	3.00	i 3.00 h	0.49	2 : 1		14	0.0	
16	3 ml 0.002 *M* $Bi(NO_3)_3$	10	Atropine	0.002	3.00	i 3.00 h	0.86	1 : 1		12	0.0	

i = intersection point; h = horizontal maximum density line.

TABLE III General composition: *a* ml *k* *M* $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + *b* ml 1 *M* nitrog

Expt. No.	*Composition*			*Molarit of KJ*
1	10 ml 0.01 *M* Nitron	+ 9 ml H_2O + (1 ml 0.5 *M* H_2SO_4)		0.5
2	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	+ 4 ml 0.001 *M* Nitron	+ 11 H_2O	0.01
3	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	+ 4 ml 0.0005 *M* Nitron	+ 11 ml H_2O	0.005
4	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4)	+ 4 ml 0.0005 *M* Nitron	+ 11 ml H_2O	0.01
5	4 ml 0.0005 *M* $Bi(NO_3)_3$ + (1 ml 0.5 *M* H_2SO_4	+ 4 ml 0.01 *M* Nitron	+ 11 ml H_2O	0.005
6	5 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.00084 *M* Sparteine	+ 1 ml H_2O	0.01
7	5 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Sparteine		0.01
8	5 ml 0.0005 *M* $Bi(NO_3)_3$	+ 3 ml 0.01 *M* Acriflavine	+ 1 ml H_2O	0.0062
9	5 ml 0.005 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Acriflavine	+ 1 ml H_2O	0.0062
10	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Rivanol	+ 13 ml H_2O	0.0062
11	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Papaverine	+ 3 ml H_2O	0.0062
12	4 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Papaverine	+ 1 ml H_2O	0.01
13	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.001 *M* Strychnine	+ 3 ml H_2O	0.0062
14	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.002 *M* Strychnine	+ 3 ml H_2O	0.0062
15	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.0005 *M* Quinine	+ 13 ml H_2O	0.0062
16	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.01 *M* Quinine	+ 3 ml H_2O	0.0062
17	3 ml 0.00125 *M* $Bi(NO_3)_3$	+ 3 ml 0.00125 *M* Phenanthroline	+ 3 ml H_2O	0.0062
18	3 ml 0.00125 *M* $Bi(NO_3)_3$	+ 4 ml 0.004 *M* Phenanthroline	+ 2 ml H_2O	0.005
19	3 ml 0.00125 *M* $Bi(NO_3)_3$	+ 3 ml 0.00063 *M* Phenanthroline	+ 3 ml H_2O	0.0062
20	3 ml 0.001 *M* $Bi(NO_3)_3$	+ 3 ml 0.0005 *M* Cinchonine	+ 13 ml H_2O	0.01
21	4 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Cinchonine	+ 11 ml H_2O	0.01
22	3 ml 0.00167 *M* $Bi(NO_3)_3$	+ 4 ml 0.00125 *M* Antipyrine	+ 2 ml H_2O	0.01
23	3 ml 0.00167 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Antipyrine	+ 2 ml H_2O	0.01
24	3 ml 0.00333 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Antipyrine	+ 2 ml H_2O	0.02
25	3 ml 0.002 *M* $Bi(NO_3)_3$	+ 3 ml 0.002 *M* Atropine	+ 3 ml H_2O	0.025
26	3 ml 0.002 *M* $Bi(NO_3)_3$ + (2 ml 0.1 *M* Na_3-citrate)	+ 3 ml 0.002 *M* Atropine	+ 2 ml H_2O	0.025
27	4 ml 0.001 *M* $Bi(NO_3)_3$	+ 4 ml 0.01 *M* Atropine	+ 1 ml H_2O	0.01

i = intersection point; h = horizontal maximum density line.

TABLE IV INTERMEDIATES A

Nitrogen compound	+ *x Bi*
	Compounds of molar ratio [Bi] : [A]
Nitron	2 : 3↓ → 1 : 1↓ → 3 : 2↓ → 2 : 1
Sparteine	2 : 3↓ → 1 : 1↓ → 3 : 2↓ → 2 : 1
Chinine	1 : 1↓ → 3 : 2↓ → 2 : 1
Cinchonine	. . . . → 2 : 1
Antipyrine	1 : 1↓ → 2 : 1↓↓
Pyramidon	1 : 1↓ → 3 : 2↓ → 2 : 1↓ → 3 : 1
Strychnine	1 : 2↓ → 3 : 4↓ → 1 : 1
Rivanol	1 : 2↓ → 2 : 3↓ → 1 : 1↓↓
Papaverine	2 : 3↓ → 1 : 1↓↓
Acriflavine	1 : 2↓ → 1 : 1↓↓
Phenanthroline	1 : 2↓ → 1 : 1↓↓
Atropine	. . . → 1 : 1↓↓

A = N-compound.

ompound + ad 10 (or ad 20) water + x *m* *M* KJ. T = 20°. Filter: red.

KJ								
Initial p.p.t.								
at ml	*molar ratio [Bi] : [J⁻]*	*ml at end-point*	*ml calculated*	*% error*	*Optical density at max.*	*Molar ratio [Bi] : [J⁻]*	*Titration time in min*	*Remarks*
		>5.0			0.0			Blank: no precipitation.
1.4	1 : 7	i 4.00 h	4.00	0.0	0.54	1 : 20	14	
3.2		>5.0			>0.37			No end-point
1.8	∼1 : 10	i 4.00 h	4.00	0.0	0.43	1 : 20	12	
0.8	1 : 2	i 4.00 h	4.00	0.0	0.84	1 : 10	14	
2.2	∼1 : 4	i 3.90 h	4.00	2.5	0.14	1 : 8	12	
1.1	1 : 2	i 4.00 h	4.00	0.0	0.88	1 : 8	12	
0.9	1 : 2	i 3.20 h	3.20	0.0	0.61	1 : 8	14	
0.5	1 : 1	i 3.20 h	3.20	0.0	0.80	1 : 8	14	
0.8	∼1 : 2	i 3.82 h	3.84	0.5	0.73	1 : 8	14	
0.9	1 : 2	i 3.80 h	3.84	1.0	0.65	1 : 8	12	
0.3		i 3.20 h	3.20	0.0	0.60	1 : 8	12	
2.3	∼1 : 5	i 3.86 h	3.84	0.5	0.5	1 : 8	14	
0.9	1 : 2	i 3.80 h	3.84	1.0	0.68	1 : 8	12	
		>5.0			0.0			
2.1	∼1 : 4	i 3.83 h	3.84	0.1	0.46	1 : 8	12	
0.2		i 2.40 h	2.40	0.0	0.78	1 : 4	12	
0.2		i 3.00 h	3.00	0.0	0.84	1 : 4	14	
2.9		>4.0			0.16		10	Too low optical densities
		>5.0			0.0			
1.6	1 : 4	i 3.20 h	3.20	0.0	0.81	1 : 8	14	
2.9		>4.0		0.13			20	Too low optical densities
0.8	∼1 : 2	i 4.00 h	4.00	0.0	0.82	1 : 8	15	
0.6		i 3.93 h	4.00	1.7	0.84	1 : 8	14	
0.8	∼1 : 4	i 1.90 h	1.92	0.5	0.60	1 : 8	12	
		>5.0		0.0				
0.9	1 : 2	i 3.20 h	3.20	0.0	0.75	1 : 8	12	

INAL COMPOUNDS

+ x Nitrogen compound	*+ x KI*
Compounds of molar ratio [Bi] : [A]	*Compounds of molar ratio [Bi] : [I]*
: 1↓ → 3 : 2↓ → 1 : 1↓↓	1 : 8↓ → 1 : 10↓↓ (in excess of nitrogen comp.)
	→ 1 : 20↓↓
: 1↓ → 2 : 1↓↓	1 : 8 ↓↓
: 1↓ → 2 : 1↓↓	1 : 6↓ → 1 : 8 ↓↓
: 1↓ → 2 : 1↓↓	1 : 8 ↓↓
: 1↓ → 1 : 1↓↓	1 : 4↓ → 1 : 8 ↓↓
: 1↓ → 3 : 1↓ → 2 : 1↓ → (3 : 2↓) → 1 : 1↓↓	(1 : 2↑) → 1 : 4 ↓ → 1 : 8↓↓
	1 : 2↑ → 1 : 4↓↓ (in excess of nitrogen comp.)
3 : 2↓ → 1 : 1↓↓	→ 1 : 8 ↓↓
3 : 2↓ → 1 : 1↓↓	1 : 4↓ → 1 : 8 ↓↓
3 : 2↓ → 1 : 1↓↓	1 : 4↓ → 1 : 6↓ → 1 : 8↓↓
3 : 2↓ → 1 : 1↓↓	1 : 4↓ → 1 : 8 ↓↓
3 : 2↓ → 1 : 1↓↓	→ 1 : 4↓↓
2 : 1↓ → 1 : 1↓↓	→ 1 : 8↓↓

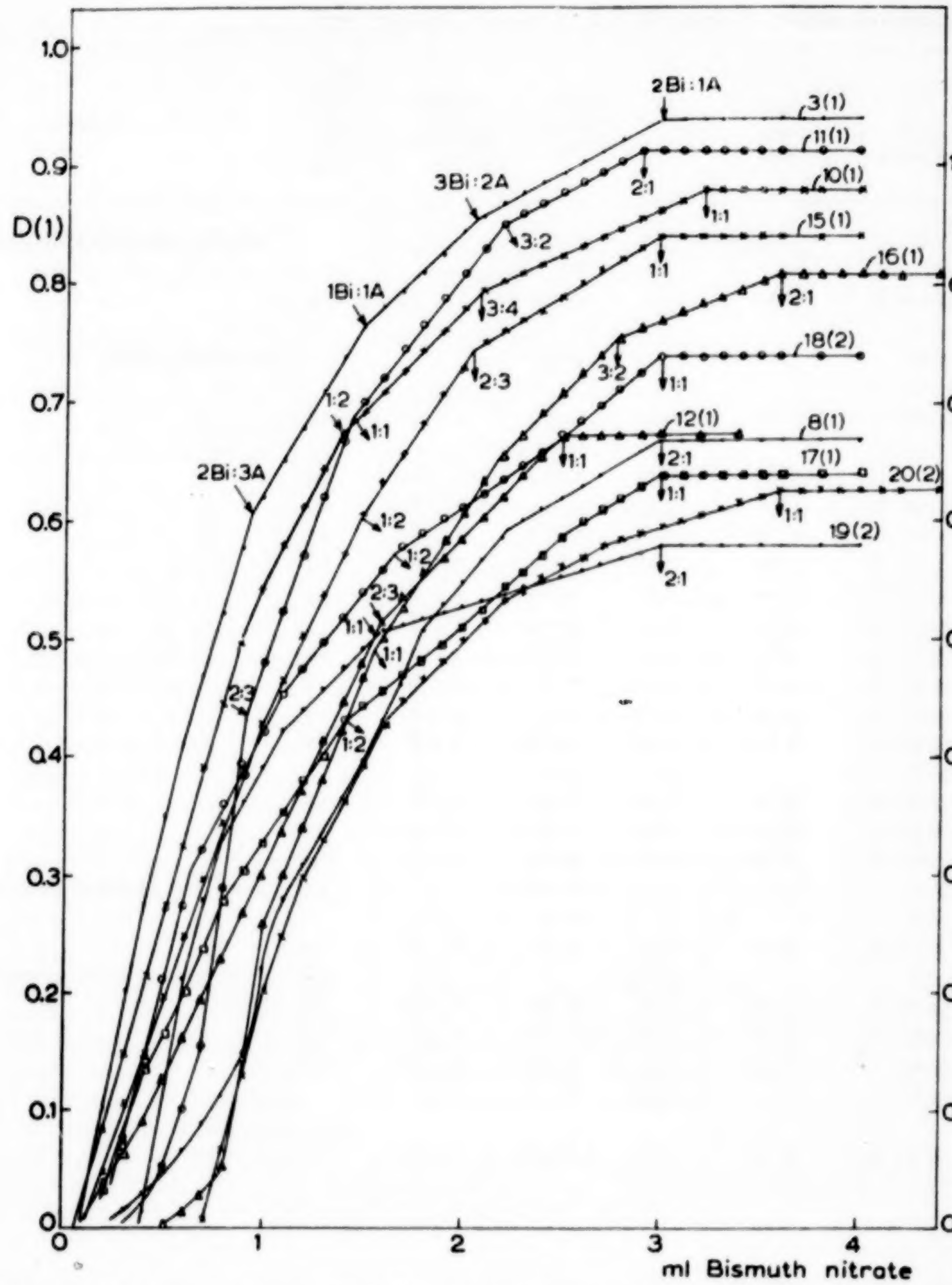


Fig. 1. Titrations of nitrogen compound (= A) with bismuth nitrate (= Bi). Molar ratios [Bi] : [A] found at the critical points. Nitrogen compound: (3) Nitron; (6) Quinine; (8) Cinchonine; (10) Strychnine; (11) Sparteine; (12) Papaverine; (15) Rivanol; (17) Acriflavine; (18) Phenanthroline; (19) Antipyrine; (20) Atropine.

TABLE V

General composition: *a* ml nitrogen compound (= A) + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KJ + ad 10 (or 20) ml H_2O + *x* ml $Bi(NO_3)_3$.

Nitrogen compound (= A)								
Name	*Content mg*	*No. of N atoms*	*Molar concentration [A]*	*Volume titrated [vol]*	*Molar amount^a used*	*Optical density at maximum*	*End compound obtained*	*Relative sensitivity of nitrogen compound*
Nitron	0.46	4	$7.5 \cdot 10^{-5}$	20	$1.5 \cdot 10^{-6}$	0.94	Bi_2A_1	4.0
Quinine	0.48	2	$7.5 \cdot 10^{-5}$	20	$1.5 \cdot 10^{-6}$	0.81	Bi_2A_1	4.0
Cinchonine	0.44	2	$7.5 \cdot 10^{-5}$	20	$1.5 \cdot 10^{-6}$	0.67	Bi_2A_1	4.0
Sparteine	0.56	2	$1.2 \cdot 10^{-4}$	20	$2.4 \cdot 10^{-6}$	0.91	Bi_2A_1	2.5
Papaverine	0.85	1	$2.5 \cdot 10^{-4}$	10	$2.5 \cdot 10^{-6}$	0.68	Bi_1A_1	2.4
Rivanol	1.1	3	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.84	Bi_1A_1	2.0
Acriflavine	0.8	3	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.64	Bi_1A_1	2.0

TABLE V (continued)

Nitrogen compound (= A)								
Name	*Content mg*	*No. of N atoms*	*Molar concentration [A]*	*Volume titrated [vol]*	*Molar amount^a used*	*Optical density at maximum*	*End compound obtained*	*Relative sensitivity of nitrogen compound*
Strychnine	1.3	2	$4 \cdot 10^{-4}$	10	$4 \cdot 10^{-6}$	0.88	Bi_1A_1	1.5
Phenanthroline	1.0	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.84	Bi_1A_1	1.2
Pyramidon	1.0	3	$4.3 \cdot 10^{-4}$	10	$4.3 \cdot 10^{-6}$	0.65	Bi_3A_1	1.2
Antipyrine	0.94	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.68	Bi_2A_1	1.2
Atropine	1.7	1	$6 \cdot 10^{-4}$	10	$6 \cdot 10^{-6}$	0.72	Bi_1A_1	1.0

[a] mole amount $= \dfrac{[A] \times [\text{vol.}]}{1000}$.

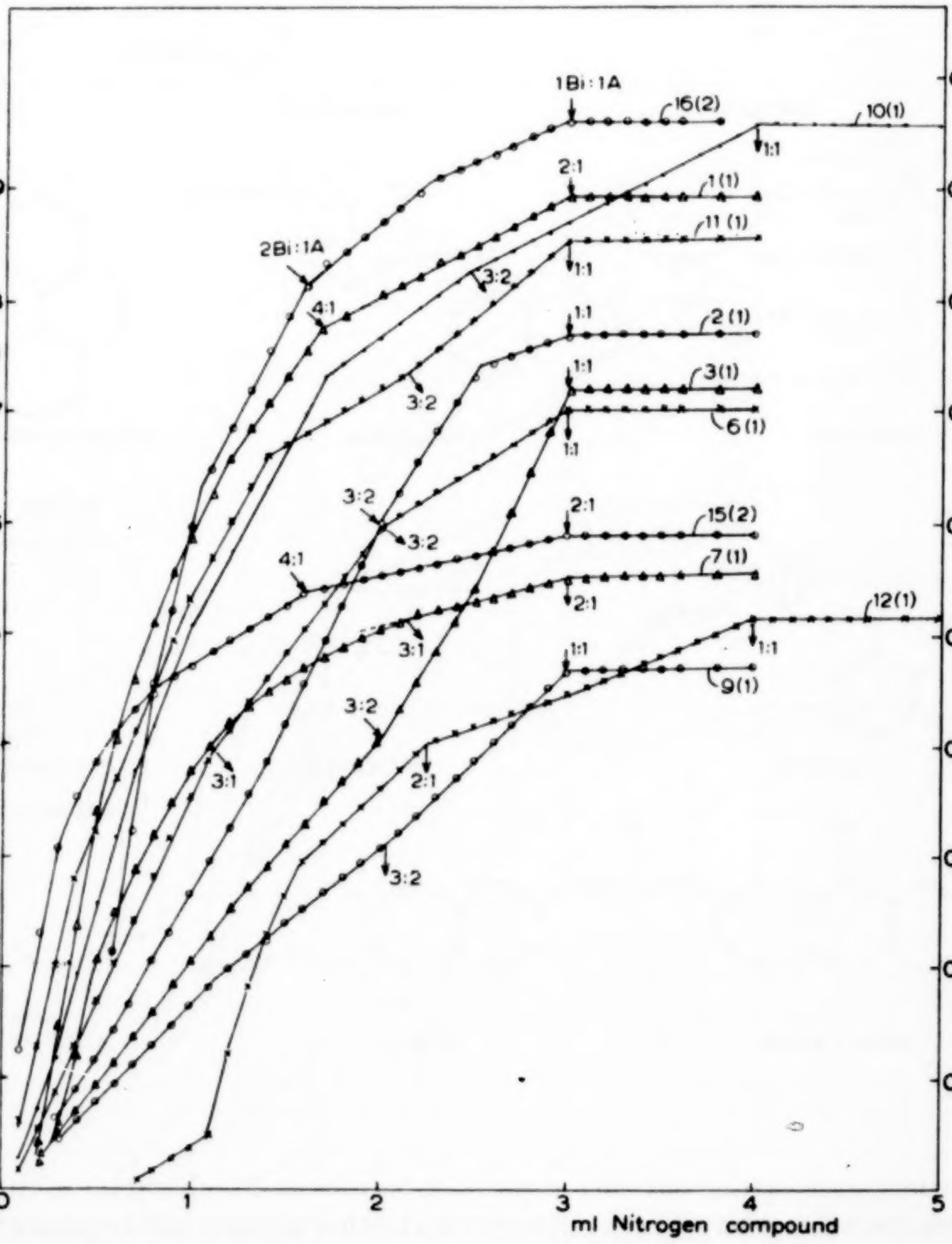
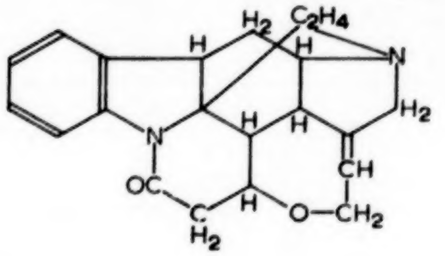


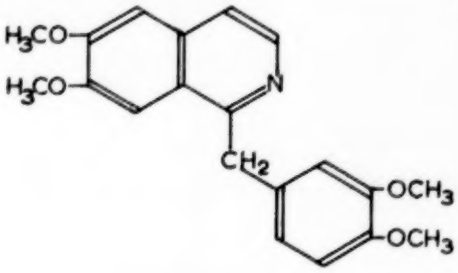
Fig. 2. Titrations of bismuth nitrate (= Bi) with nitrogen compound (= A). Molar ratios [Bi : [A] found at the critical points. Nitrogen compound: (1) Quinine; (2) Papaverine; (3) Acriflavine; (6) Nitron; (7) Cinchonine; (9) Rivanol; (10) Strychnine; (11) Phenanthroline; (12) Antipyrine; (15) Sparteine; (16) Atropine.

In this work, eleven heterocyclic nitrogen compounds were studied and twelve N-compounds were compared with one another. We present here the accepted structures for these compounds for comparison.

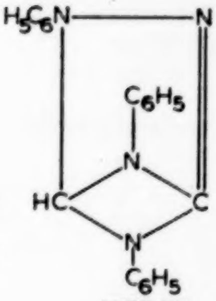
STRUCTURES OF N-COMPOUNDS



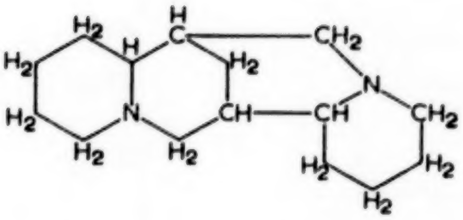
STRYCHNINE



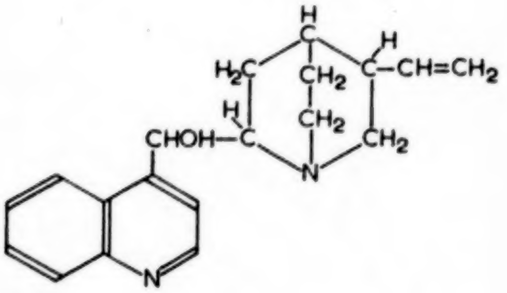
PAPAVERINE



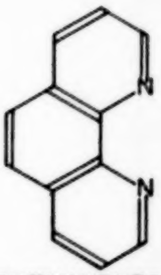
NITRON



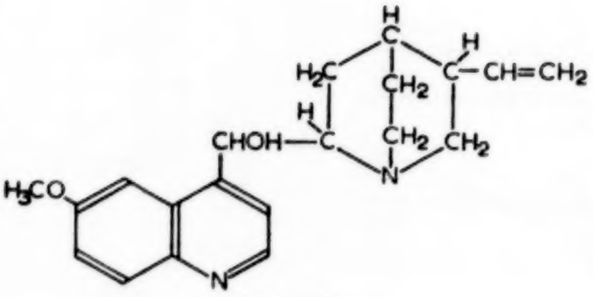
SPARTEINE



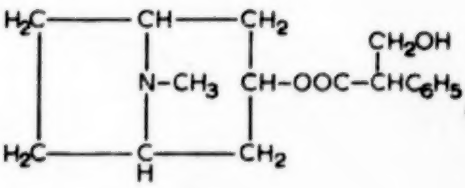
CINCHONINE



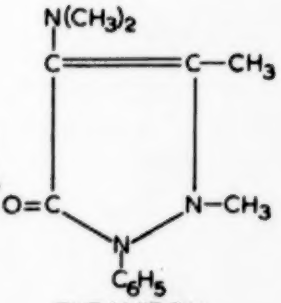
o-PHENANTHROLINE



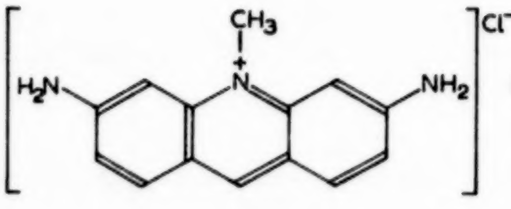
QUININE



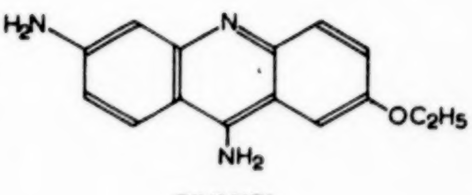
ATROPINE



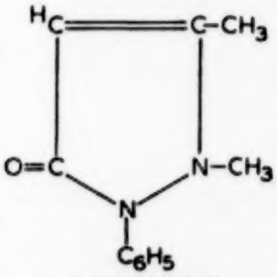
PYRAMIDON



ACRIFLAVINE



RIVANOL



ANTIPYRINE

All titrations were carried out only at pH ∼ 1, because of the character of the bismuth iodide reaction. Later on some experiments with other titrants will be presented which enabled us to study similar reactions at various pH values. If we consider the composition and the structure of the N-compounds investigated, we find that the molecules contain from *one* to *four* N-atoms. Some of the N-atoms are built in *closed* rings, the others are *external* non-methylated amino groups. We will see later that the latter are insensitive towards the reaction with bismuth iodide.

Many alkaloids, or other N-compounds, have a smaller molecular weight than those mentioned above; they were less sensitive and gave precipitations only if used in higher concentrations than usual. They were therefore not included in our study. The following belong to this group: quinoline (3 ml 0.00125 *M*), caffeine (4 ml 0.002 *M*), theobromine (4 ml 0.005 *M*), urotropine (4 ml 0.001 *M*); streptomycin (4 ml 0.5%) and benzidine (1 ml 0.01 *M*).

1. *Titrations of N-compounds with bismuth nitrate*

Tables I and IV show the composition and the results. Table V contains calculations

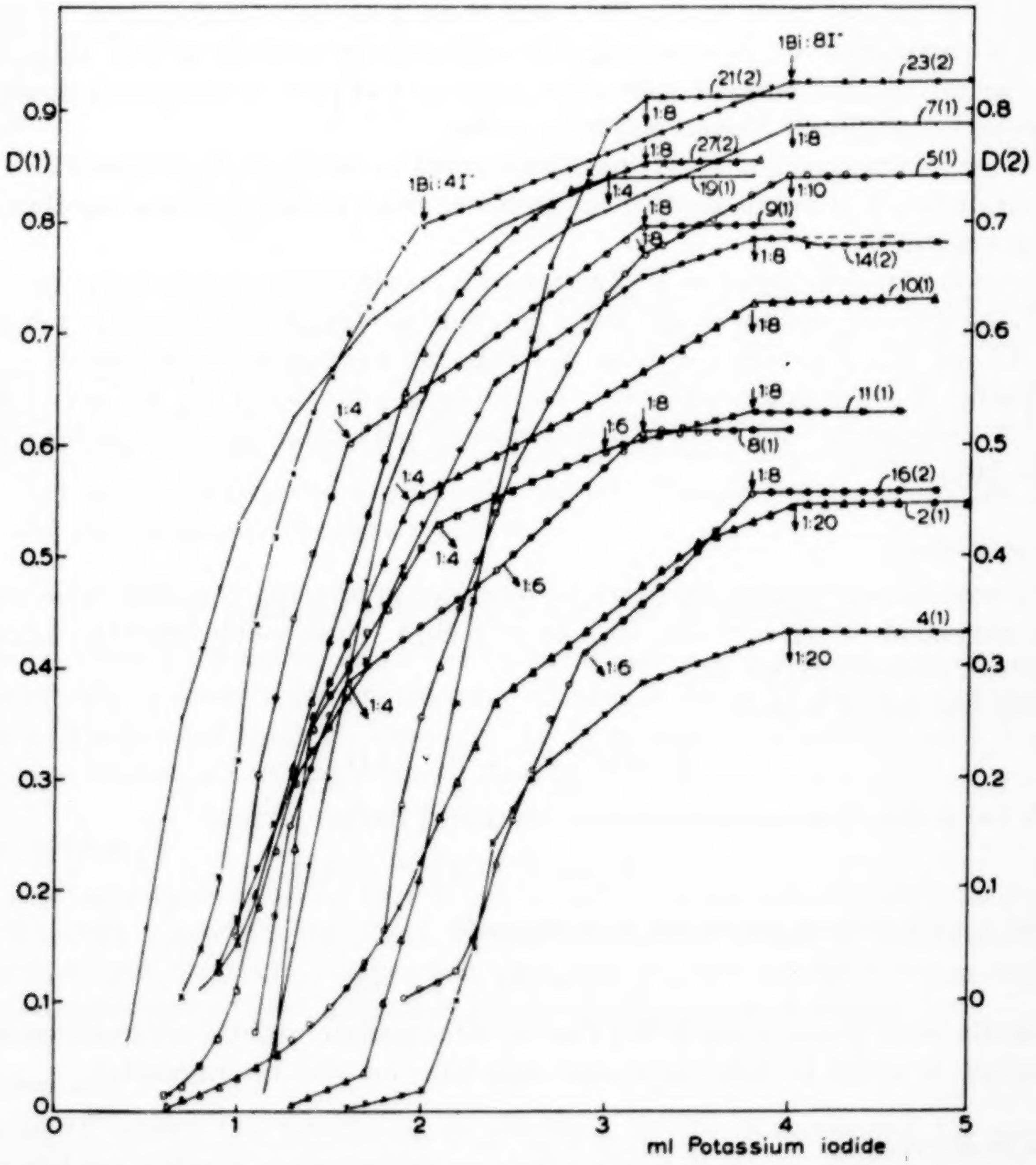


Fig. 3. Titrations of mixtures of bismuth nitrate and nitrogen compound with potassium iodide. Molar ratio [Bi] : [I⁻] found at the critical points. Nitrogen compound: (2), (4) and (5) Nitron; (7) Sparteine; (9) Acriflavine; (10) Rivanol; (11) Papaverine; (14) Strychnine; (16) Quinine; (19) Phenanthroline; (21) Cinchonine; (23) Antipyrine; (27) Atropine.

based on Table I. The course of some of these experiments (Table I) is presented in Fig. 1. In Table IV we have summarized the different intermediate and final compounds obtained in Tables I–III.

Compounds

Final compounds

A glance at Tables I and IV shows that only *two* final compounds $Bi_2A\downarrow\downarrow$ and $BiA\downarrow\downarrow$ were ever obtained by titrating N-compounds ,with the exception of pyramidon, with bismuth nitrate. The compound $Bi_2A\downarrow\downarrow$ was always obtained if at least *two* N-atoms were built into the cyclic aromatic or aliphatic compound. Phenanthroline and strychnine were exceptions and gave $BiA\downarrow\downarrow$ instead. Evidently in phenanthroline, the two nitrogen atoms, although having similar construction, could not act separately with the bismuth iodide anion. In strychnine, one of the two nitrogen atoms is inactive, so that this alkaloid must be classified with those with one nitrogen atom. Both the above N-compounds act as *mono*basic N-compounds. In contrast to this, antipyrine, with two nitrogen atoms near each other, acted as a *di*-basic N-compound giving the compound $Bi_2A\downarrow\downarrow$ *with bismuth nitrate as titrant.*

Quinine, cinchonine and sparteine *always* acted as *two*-basic N-compounds. These all contain *two* N-atoms in aliphatic or aromatic rings, *distant* from one another, and acting separately.

Nitron is now considered as a "Zwitterion"; its electronic structure has not been finally established, and we do not know how the charges are distributed in the molecule. In any case it acts as a *di*-basic N-compound *when titrated with bismuth.*

All other N-compounds contain only one nitrogen atom in the ring and act as *mono*-basic N-compounds. Such is the case with rivanol and acriflavine which have external amino groups.

Intermediates

The sequences of intermediates traced remained in principle the same, whether the final compound ($= \downarrow\downarrow$) was BiA, Bi_2A or even Bi_3A. Thus, we obtained the following sequences of molar ratios [Bi] : [A].

With one active N-atom:

$$1 : 2\downarrow \rightarrow 2 : 3\downarrow \rightarrow 1 : 1\downarrow\downarrow$$

With *two* active N-atoms the sequence continued further giving:

$$. \quad . \quad . \; 1 : 1\downarrow \rightarrow 3 : 2\downarrow \rightarrow 2 : 1\downarrow\downarrow$$

In the special case of pyramidon it continued:

$$. \quad . \quad . \; 2 : 1\downarrow \rightarrow 3 : 1\downarrow\downarrow$$

Evidently there is even a possibility that an intermediate with the composition $BiA_2\downarrow$ is formed. It would be risky to present structures for such intermediates.

Analytical aspects

Sensitivity. Table V contains calculations carried out on the basis of table 1 which show us the sensitivity of the alkaloid titrations with bismuth nitrate. The reaction is most sensitive with N-compounds containing two *separate* ring systems in the mole-

TABLE VI

General composition: *a* ml $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + 2 ml 0.1 *M* KJ + ad 10 (or 20) ml H_2O + *x* ml nitrogen compound (= A)

Nitrogen compound		*$Bi(NO_3)_3$*					
Name	*No. of N atoms*	*Molar concentration [Bi]*	*Vol. titrated [vol] (ml)*	*Molar amount[a] of bismuth nitrate*	*Optical density at max.*	*End compound obtained*	*Relative sensitivity of nitrogen compound*
Quinine	2	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.89	Bi_2A_1	2
Papaverine	1	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.77	Bi_1A_1	2
Acriflavine	3	$3 \cdot 10^{-4}$	10	$3 \cdot 10^{-6}$	0.72	Bi_1A_1	2
Nitron	4	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.69	Bi_1A_1	2
Cinchonine	2	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.55	Bi_2A_1	2
Rivanol	3	$1.5 \cdot 10^{-4}$	20	$3 \cdot 10^{-6}$	0.47	Bi_1A_1	2
Strychnine	2	$4 \cdot 10^{-4}$	10	$4 \cdot 10^{-6}$	0.96	Bi_1A_1	1.5
Pyramidon	3	$4 \cdot 10^{-4}$	10	$4 \cdot 10^{-6}$	0.66	Bi_1A_1	∼1.5
Phenanthroline	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.85	Bi_1A_1	1.2
Antipyrine	2	$5 \cdot 10^{-4}$	10	$5 \cdot 10^{-6}$	0.51	Bi_1A_1	1.2
Sparteine	2	$2.5 \cdot 10^{-4}$	20	$5 \cdot 10^{-6}$	0.49	Bi_2A_1	1.2
Atropine	1	$6 \cdot 10^{-4}$	10	$6 \cdot 10^{-6}$	0.86	Bi_1A_1	1.0

[a] mole amount $= \frac{[Bi] \times [vol]}{1000}$.

cule, each with one nitrogen atom. These are quinine and cinchonine. The reaction is also sensitive towards nitron. The sensitivity is about four times as high as with atropine. Second in sensitivity come the *large* N-compounds containing one active N-atom in the molecule. These are sparteine and papaverine. They are about 2.5 times as sensitive as atropine. Rivanol and acriflavine act with *one* nitrogen atom in the ring, they are about twice as sensitive as atropine. Phenanthroline, antipyrine, atropine and pyramidon are the least sensitive.

2. *Titrations of bismuth nitrate with N-compounds*

Table II presents a selection of such experiments, their composition and the results obtained. Fig. 2 shows the course of some titrations. Table VI contains calculations made on the basis of Table II. Generally the differences in the results, using N-compounds as titrant, are less pronounced than in Table V.

Final compounds

It is interesting to establish that in only a very few cases a final compound Bi_2A↓↓ was obtained. These are the three alkaloids discussed separately before: quinine, cinchonine and sparteine. Compounds with two or more cyclic N-atoms such as nitron, antipyrine and phenanthroline, all gave final compounds BiA↓↓.

Intermediates

Table IV shows the intermediates obtained. If the N-compound (= titrant) contained *two* active N-atoms we obtained the sequence:

$$4 : 1\downarrow \rightarrow 2 : 1\downarrow\downarrow$$

$$\text{or } 2 : 1\downarrow \rightarrow 1 : 1\downarrow\downarrow \text{ (antipyrine)}$$

but if only *one* N-atom was active:

$$3 : 2\downarrow \rightarrow 1 : 1\downarrow\downarrow$$

Molecules with more than *two* nitrogen in the molecule (such as nitron or pyramidon) gave more intermediates:

Pyramidon: $4 : 1\downarrow \rightarrow 3 : 1\downarrow \rightarrow 2 : 1\downarrow \rightarrow 3 : 2\downarrow : \downarrow \rightarrow 1 : 1\downarrow\downarrow$
Nitron: $3 : 1\downarrow \rightarrow 3 : 2\downarrow \rightarrow 1 : 1\downarrow\downarrow$

TABLE VII

General composition: *a* ml $Bi(NO_3)_3$ + 1 ml *M* HNO_3 + *b* ml nitrogen compound + ad 10 (or 20) ml H_2O + *x* ml KJ

Nitrogen compound		*Bi(NO₃)₃*					
Name	*No. of N atoms*	*Molar concentration [Bi]*	*Vol. titrated [vol] in ml*	*Molar amount*[a] *of bismuth nitrate*	*Optical density at max.*	*Molar ratio of [Bi] : [J⁻] at the end-point*	*Relative sensitivity of nitrogen compound*
Nitron	4	$1\cdot10^{-4}$	20	$2\cdot10^{-6}$	0.43	1 : 20	3.0
Sparteine[b]	2	$2.5\cdot10^{-4}$	10	$2.5\cdot10^{-6}$	0.89	1 : 8	2.4
Acriflavine	3	$2.5\cdot10^{-4}$	10	$2.5\cdot10^{-6}$	0.80	1 : 8	2.4
Rivanol	3	$1.5\cdot10^{-4}$	20	$3\cdot10^{-6}$	0.73	1 : 8	2.0
Papaverine	1	$3\cdot10^{-4}$	10	$3\cdot10^{-6}$	0.63	1 : 8	2.0
Strychnine	2	$3\cdot10^{-4}$	10	$3\cdot10^{-6}$	0.48	1 : 8	2.0
Quinine[b]	2	$3\cdot10^{-4}$	10	$3\cdot10^{-6}$	0.46	1 : 8	2.0
Phenanthroline	2	$3.75\cdot10^{-4}$	10	$3.75\cdot10^{-6}$	0.78	1 : 4	1.6
Cinchonine[b]	2	$2\cdot10^{-4}$	20	$4\cdot10^{-6}$	0.81	1 : 8	1.5
Pyramidon	3	$5\cdot10^{-4}$	10	$5\cdot10^{-6}$	0.42	1 : 8	>1.2
Antipyrine	2	$5\cdot10^{-4}$	10	$5\cdot10^{-6}$	0.13	1 : 8	1.2
Atropine	1	$6\cdot10^{-4}$	10	$6\cdot10^{-6}$	0.60	1 : 8	1.0

[a] mole amount $= \dfrac{[Bi] \times [vol]}{1000}$.

[b] Alkaloid present in large excesses.

Analytical aspect

Table VI contains calculations concerning the sensitivity of the bismuth determination using different N-compounds. The variations in sensitivity are relatively small. Thus, using atropine as titrant, the amount of bismuth analysed had only to be doubled in comparison with the action with quinine or nitron. The errors shown in Table II were equally negligible using the different N-compounds as titrant. 0.3–0.5 mg of bismuth were necessary for the determination.

3. *Titrations of bismuth nitrate with potassium iodide*

Tables III, IV and VII and Fig. 3 present the experiments made, the bismuth–iodo complexes obtained and the calculations of sensitivity.

Compounds

Final compounds. In the presence of almost all the N-compounds used, the final molar ratio of [Bi] : [I⁻] was 1 : 8. Only phenanthroline behaved differently, giving a final ratio of 1 : 4$\downarrow\downarrow$. The nitron also behaved differently, giving 1 : 10$\downarrow\downarrow$ in excess of nitron, and if less nitron was used, the final ratio was 1 : 20$\downarrow\downarrow$. Working in excess of pyramidon, the final compound was also obtained at the ratio of 1 : 4↓↓. With sparteine, quinine and cinchonine, the final compound had the composition 1 : 8↓↓ if an excess of alkaloid was used.

Intermediates. The number of intermediates was relatively small. Thus, in general, the following sequences were traced:

1 : 4↓ → 1 : 8↓↓
1 : 2↑ → 1 : 4↓↓

The intermediate 1 : 2 was always soluble.

Sensitivity

The sensitivity in relation to bismuth was different than that towards the N-compound used. The variations in sensitivity towards bismuth were relatively small when using different alkaloids. The same was the case if the sensitivity towards the different alkaloids was compared (Table VII).

METHOD

0.5–1 mg of alkaloid in 10 (or 20) ml aqueous solution, containing 1 ml *M* HNO_3 and 2 ml 0.1 *M* KI, are titrated with 0.001–0.0015 *M* bismuth nitrate.

Remark: In the case of the less sensitive alkaloids, more of the alkaloid must be taken. The first maximum density point lies at BiA↓↓. Using quinine, cinchonine, sparteine or antipyrine, the end-point lies at Bi_2A↓↓.

SUMMARY

The reactions between nitron, quinine, cinchonine, strychnine, sparteine, papaverine, rivanol, acriflavine, phenanthroline, antipyrine and atropine with bismuth nitrate in potassium iodide solution were studied heterometrically. The individual structure of the N-compounds was discussed on the basis of the reactions and the large salt-compounds obtained. 0.5 to 1 mg of N-compound was necessary for a determination which lasted 10–15 min. The errors in almost all cases were negligible. 0.3–0.5 mg bismuth could also be determined by the titration of bismuth with N-compounds and the error was negligible.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique des réactions de divers alcaloïdes avec le nitrate de bismuth et l'iodure de potassium. On a pu ainsi établir une méthode de titrage des alcaloïdes et également une méthode de titrage du bismuth.

ZUSAMMENFASSUNG

Die Reaktion einer Anzahl Alkaloide mit Wismutnitrat in Gegenwart von Jodkalium wurde heterometrisch untersucht. Sie lässt sich zur titrimetrischen Bestimmung von Wismut bezw. Alkaloiden verwenden.

REFERENCES

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[2] M. Bobtelsky and J. Eisenstaedter, *Anal. Chim. Acta*, 20 (1959) 216, 357.
[3] M. Bobtelsky, *Anal. Chim. Acta*, 13 (1955) 172.

DÉTECTION ET DOSAGE DE TRÈS PETITES QUANTITÉS D'EAU PAR LA MÉTHODE HYGROPHOTOGRAPHIQUE

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(Reçu le 19 juin 1959)

L'hygrophotographie, dont le principe est basé sur l'emploi de plaques ou de films spéciaux à l'iodure d'argent et de mercure, sensibles à la fois vis-à-vis de la lumière et de l'humidité, permet de fixer sur du papier ou des plaques photographiques ordinaires la trace de l'humidité enregistrée sur la plaque hygrophotographique exposée d'abord à l'influence de la lumière et ensuite à celle de l'eau[1]. Cette trace, dont l'intensité est proportionnelle à la quantité d'eau absorbée par la couche sensible, est ensuite comparée à une échelle densitométrique obtenue au moyen de quantités d'eau exactement connues. Leur mesure est faite, ainsi que nous allons l'exposer plus loin, à l'aide d'un densitomètre et d'une balance de précision sensible au millième de milligramme.

Lorsqu'on pose une goutte d'un solvant organique neutre, contenant de l'eau, sur une feuille de papier filtre, enfermée hermétiquement entre une plaque hygrophotographique noircie au préable par exposition à la lumière et une plaque de verre ordinaire transparente, l'ensemble étant serré fortement à l'aide de ressorts (dans un châssis-presse photographique, par exemple), on voit alors que le solvant ne pouvant pas s'évaporer rapidement, s'étale librement, par absorption, dans l'épaisseur du papier filtre; quand il a atteint son étalement maximum, le solvant commence à s'évaporer lentement, à partir de la périphérie, et, lorsqu'il s'agit par exemple de

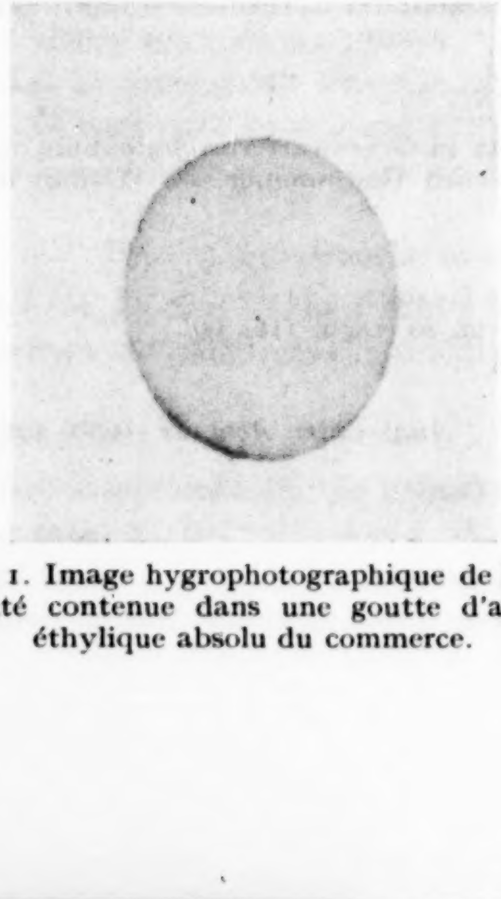

Fig. 1. Image hygrophotographique de l'humidité contenue dans une goutte d'alcool éthylique absolu du commerce.

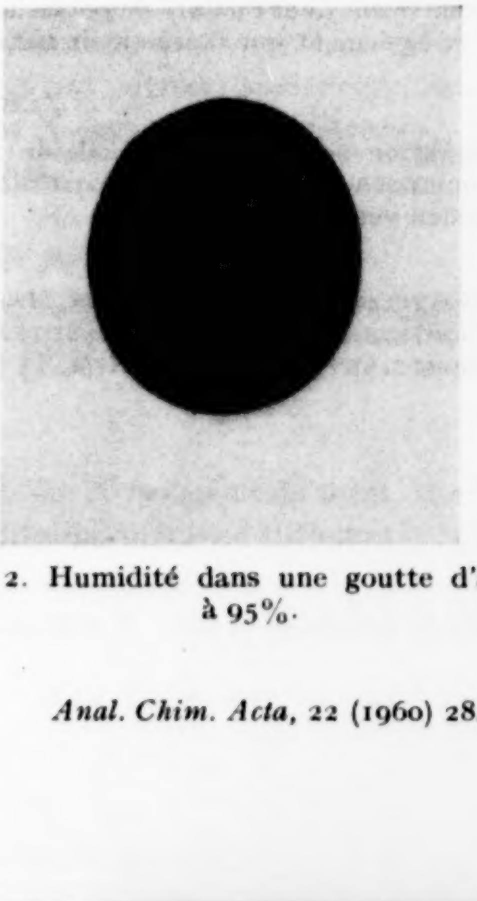

Fig. 2. Humidité dans une goutte d'alcool à 95%.

l'alcool éthylique, au fur et à mesure que s'évapore cet alcool, la très faible quantité d'eau qui peut se trouver dans la goutte passe du papier dans la gélatine et forme sur la plaque hygrophotographique, en allant de la périphérie vers le centre, une tache arrondie ou un anneau, dont l'aspect varie suivant la quantité d'eau contenue dans l'alcool.

Avec l'alcool éthylique absolu du commerce, on obtient un anneau périphérique jaune clair, ayant une partie centrale qui se détache sur la plaque hygrophotographique par une teinte moins claire et qui, sur les épreuves positives se traduit par une couleur grisâtre, alors que le cercle périphérique y figure en noir (Fig. 1). Avec les alcools à 95 et à 90%, on obtient des taches uniformément noires (Fig. 2).

Dans le cas de l'alcool méthylique, comme il est encore plus difficile d'avoir un échantillon absolument privé d'humidité, sur notre demande, M. PESEZ, dans les laboratoires de l'UCLAF, a bien voulu faire quelques essais en vue d'obtenir un méthanol rigoureusement anhydre. La méthode de déshydratation qu'il a utilisée, est l'ébullition avec du magnésium, selon BJERRUM ET ZECHMEISTER[2].

Partant d'un méthanol à 0.06% en eau, dosée par la méthode de Fischer, il a obtenu un distillat qui, recueilli dans les meilleures conditions possibles, montrait encore au dosage une teneur en eau de 0.01%. Un second traitement n'a pas fait baisser la teneur en eau. C'est avec cet échantillon que j'ai obtenu la figure 3 en mettant sur le papier filtre et à une certaine distance l'une de l'autre, deux gouttes du liquide maintenues enfermées entre la plaque hygrophotographique et la plaque transparente.

Ici, comme dans le cas de l'alcool éthylique ou des alcools propyliques, l'étalement de l'eau dans le papier filtre a lieu simultanément avec son solvant organique; le passage de cette eau du papier dans la plaque ne peut avoir lieu par conséquent qu'après l'évaporation du solvant à la limite de son étalement maximum; l'inscription de la tache humide sur la plaque se fait donc uniquement en progressant de la périphérie vers le centre, au fur et à mesure de l'évaporation (Fig. 3).

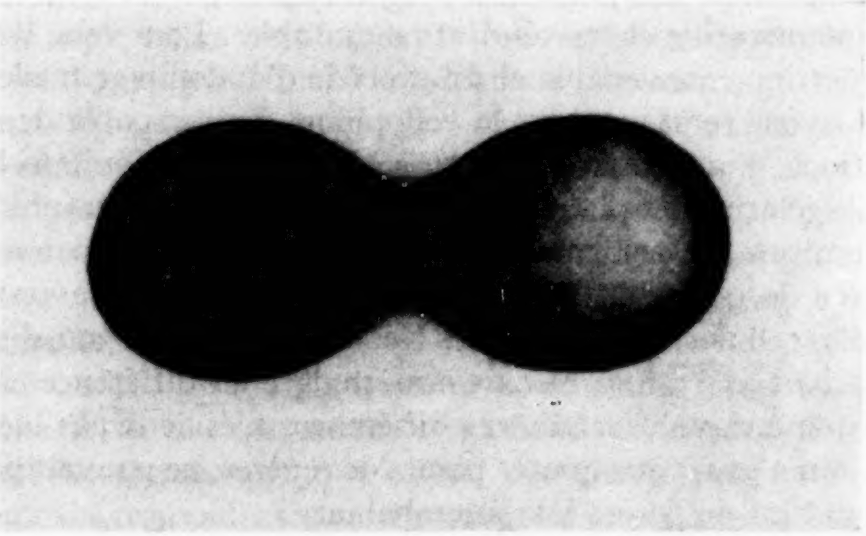

Fig. 3. Hygrophotographie obtenue avec deux gouttes d'alcool méthylique absolu distillé sur du magnésium.

Par contre, dans le cas de l'alcool butylique tertiaire, l'étalement de la goutte dans le papier filtre n'ayant pas lieu simultanément pour l'alcool et pour l'eau, en particulier si l'on a préparé deux mélanges binaires composés respectivement de 20 et de

30 parties d'eau pour 80 et 70 parties d'alcool, en volumes, dès que la goutte se trouve appliquée sur le papier et enfermée hermétiquement entre les deux plaques, elle semble s'y étaler normalement; mais en réalité, l'eau ne suit pas constamment l'étalement de l'alcool; elle reste en majeure partie au centre de l'étalement, tandis que l'alcool se porte de plus en plus vers la périphérie; au bout d'une minute, on voit alors l'eau centrale passer presque intégralement et d'un seul trait dans la gélatine en formant instantanément sur la plaque une tache jaune intense (Fig. 4), dont le diamètre est par conséquent bien inférieur à celui du liquide resté sur le papier.

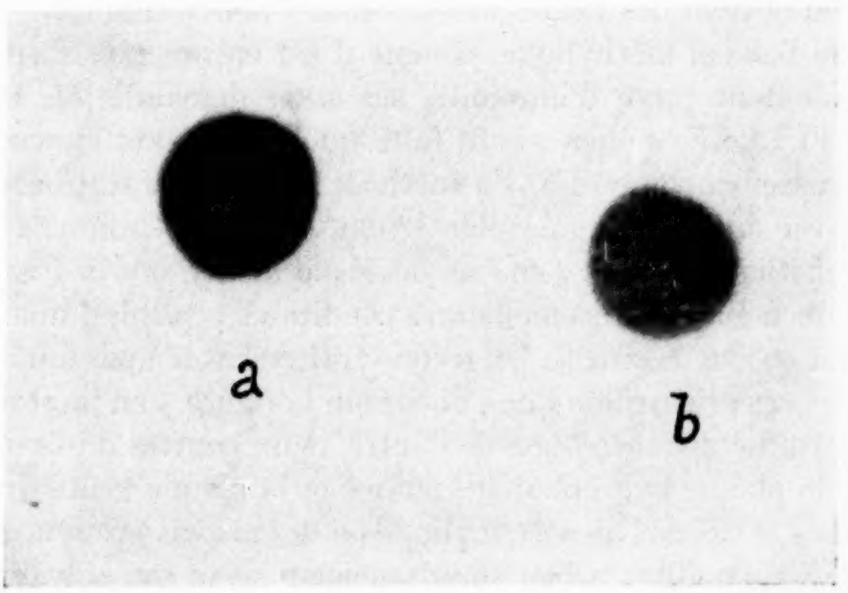

Fig. 4. Hygrophotographie de l'eau contenue dans une goutte d'alcool butylique tertiaire en: a. mélange binaire alcool-eau 7/3; b. mélange binaire 8/2. Diamètre de l'étalement maximum sur papier 2.3 × 2.7 diamètre de la tache de l'eau sur la plaque 1.5 × 1.4.

Dès nos premières applications de l'hygrophotographie à l'enregistrement et à l'étude de la transpiration des plantes, notre principale préoccupation a été de rendre cette méthode quantitative et ses résultats mesurables. Pour cela, il nous fallait une échelle densitométrique convenable et un procédé d'étalonnage facile et rapide.

Lorsque nous avons remarqué que la cellophane était capable de se saturer, dans certaines conditions, d'une quantité déterminée d'humidité, toujours la même, qu'elle cédait ensuite à la gélatine des plaques ou des films hygrophotographiques, nous avons pensé pouvoir utiliser ces pellicules cellulosiques de diverses épaisseurs et, par conséquent, chargées de quantités d'eau différentes; mais nous avons vite remarqué qu'avec les feuilles cellulosiques naturelles No. 600, 500, 400 et 300, dont les épaisseurs respectives sont 0.02, 0.03, 0.04 et 0.05 mm, malgré les différences indéniables dans la gamme densitométrique obtenue, ces différences n'étaient pas bien tranchées; en outre, l'échelle, qui n'avait que quatre points de repères, ne pouvait pas être complète et elle exigeait autant de pesées à la microbalance.

Finalement, nous avons pu construire une échelle densitométrique, correspondant à six degrés de décolorations obtenues avec des quantités déterminées d'eau de plus en plus faibles, en utilisant pour cela, en plus de l'eau pure, cinq solutions de bromure de sodium à (1, 2.5, 3, 4.5 et 5 M), solutions dont les tensions de vapeur, à la température de 25°, ont été déterminées avec un très grand soin par PEARCE, TAYLOR et BARTLETT[3].

Un calcul simple permet de ramener cette tension de vapeur à celle de la température du laboratoire au moment de l'expérience.

Comme

$$p = p_0(1 + \alpha t),$$

on a par conséquent

$$p_0 = \frac{p}{1 + \alpha t},$$

dans laquelle $\alpha = 0.003662$.

Dans le cas qui nous occupe, p_0 est la tension de vapeur des solutions à la température du laboratoire, 22° au moment de l'étalonnage et p, celle qui est donnée dans les tables des auteurs cités pour la température de 25°, donc $t = 25 - 22° = 3°$.

Ainsi, on trouve

$$\frac{p}{1 + 0.003662 \times 3} = \frac{22.973}{1.010986} = 22.723 \text{ mm}$$

pour la tension de vapeur, à 22°, de la solution à une molécule de bromure de sodium par litre, dont la tension de vapeur à 25° est 22.973 mm, d'après la détermination des auteurs précités.

Pour le calibrage de l'échelle densitométrique constituée de cette manière, nous avons pris un petit flacon de 8–10 ml environ, muni d'un couvercle souple et hermétique, et rempli de moitié avec de l'eau distillée.

On recouvre l'ouverture de ce flacon avec une feuille de cellophane naturelle, c'est-à-dire non imperméabilisée, (No. 600), trempée dans l'eau et on la fixe au goulot du flacon à l'aide d'un fil de coton. On la laisse sécher à l'air, on coupe et on enlève les parties de la pellicule cellulosique qui dépassent l'enroulement du fil et on bouche de nouveau le flacon avec son couvercle souple en plastique.

En conservant le récipient ainsi bouché pendant plusieurs heures, la vapeur dégagée par l'eau contenue dans celui-ci est absorbée au fur et à mesure par la cellophane qui se sature d'humidité. Nous estimons qu'une période de 24 heures de repos est largement suffisante pour obtenir l'état de saturation exigé pour le calibrage.

Lorsque, après avoir retiré rapidement le couvercle, on applique immédiatement sur l'ouverture du flacon, pendant trois minutes exactement, et en la pressant avec un poids convenable, une plaque hygrophotographique, l'humidité contenue dans la cellophane passe dans la gélatine de la plaque en y produisant une zone arrondie de décoloration. En pesant le flacon bouché avant et après cette opération, on peut connaître exactement la quantité d'eau cédée par la cellophane à la plaque. La pellicule cellulosique se comporte ici comme un condensateur qui se charge d'électricité et se décharge ensuite.

Connaissant la surface de décoloration et la quantité d'eau absorbée par cette surface, il est facile de calculer la quantité d'eau fixée par unité de surface de la plaque.

On place ensuite cette même plaque sur un bloc transparent en plexiglas, portant dans son épaisseur six creux identiques arrondis, de 8 mm de profondeur et de 10 mm de largeur, remplis successivement de l'eau pure et de cinq solutions de bromure de sodium, de concentrations croissantes et on y maintient celle-ci, sous une pression suffisante, jusqu'à ce que la décoloration obtenue avec l'eau pure soit identique à celle produite par la cellophane, ce qui demande de 10 à 15 min. L'égalité des décolorations peut d'ailleurs être établie avec l'une quelconque des cinq solutions salines du bloc.

Quand cette égalité est obtenue, cela indique que la quantité de vapeur d'eau absorbée par la partie de la plaque au-dessus de l'eau pure est telle qu'elle a fixé, par unité de surface, une quantité d'eau égale à celle fixée sur la zone de comparaison.

Ici, le diamètre de cette zone imprimée par la cellophane et qui est rendue en noir sur les images positives, étant de 21 mm, sa surface est de 346.36 mm²; la quantité d'eau absorbée par cette surface est de 3169 µg dans une première pesée, et de 3193 µg dans une seconde. On voit que cette quantité est à peu près constante, ce qui permet de ne pas avoir recours constamment à la balance, lorsqu'on travaille surtout loin du laboratoire. Le calcul montre que la quantité d'eau fixée est de 9.1 µg et de 9.2 µg par mm² de surface.

Si une mole d'eau pure (18 g), à la pression atmosphérique (760 mm) occupe 22,400 cm³, 0.0000091 g d'eau pure doit occuper

$$\frac{22{,}400 \times 0.0000091}{18} = 0.0113 \text{ cm}^3.$$

La tension de vapeur de l'eau pure, à 25°, étant 23.752 mm, à 22° elle est 23.493 mm et comme 9.1 µg d'eau sous 760 mm occupe un volume de 0.0113 cm³, sous 23.493 mm, elle occupe

$$\frac{0.0113 \times 760}{23.493} = 0.3655 \text{ cm}^3.$$

D'autre part, dans l'échelle densitométrique ainsi constituée (Fig. 5), le degré densitométrique de la figure 5a témoin, obtenue avec la pellicule cellulosique, étant identique à celui de la figure 5b, qui correspond à l'eau pure, la quantité d'eau fixée par unité de surface pour cette figure est donc 9.1 µg par mm².

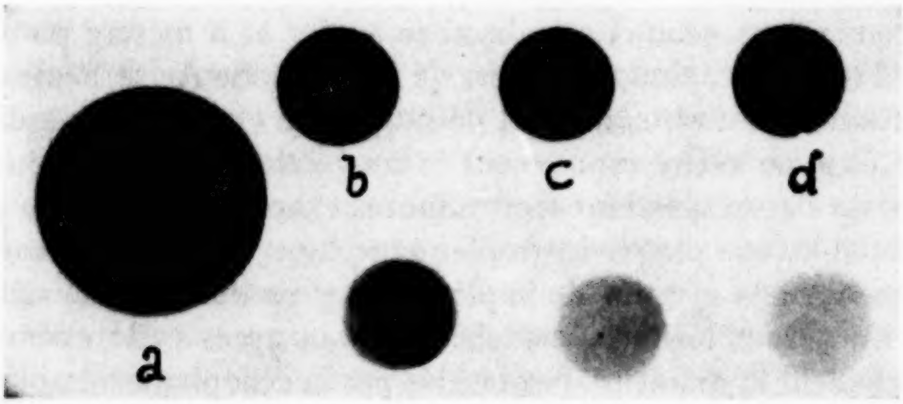

Fig. 5. Échelle densitométrique établie avec de l'eau pure (en a et en b) et de 5 solutions de bromure de sodium de concentrations croissantes.

Mais, si sous une tension de 23.493 mm, on a obtenu l'évaporation de 0.3655 cm³ d'eau, sous 19.289 mm (tension de vapeur, à 22°, de la solution de bromure de sodium 4.5 *M*), on a dû obtenir l'évaporation de

$$\frac{19.289 \times 0.3655}{23.493} = 0.3008 \text{ cm}^3$$

d'eau et comme 0.3655 cm³ d'eau pèse 9.1 µg, 0.3008 cm³ d'eau pèse

$$\frac{0.3008 \times 9.1}{0.3655} = 7.4 \ \mu\text{g}.$$

Un raisonnement analogue nous montre que sous une tension de vapeur de 18.671 mm, qui est celle de la solution de bromure de sodium 5 *M* pour la même température, la plaque hygrophotographique a dû absorber 0.2904 cm³ de vapeur d'eau, d'un poids de 7.2 µg.

Le calcul final donne les résultats suivants:

TABLE I

	Tension de vapeur à 22°	*Vapeur dégagée en*	
		cm³	*µg*
Eau pure	23.493	0.3655	9.1
BrNa, *M*	22.723	0.3535	8.8
BrNa, 2.5 *M*	21.435	0.3334	8.3
BrNa, 3 *M*	20.950	0.3259	8.1
BrNa, 4.5 *M*	19.289	0.3008	7.4
BrNa, 5 *M*	18.671	0.2904	7.2

La comparaison des enregistrements hygrophotographiques obtenus au contact des échantillons soumis à l'analyse (feuille végétale, terre arable, matières plastiques, etc.) à l'échelle densitométrique peut être faite par simple examen à l'oeil nu, mais elle peut aussi être effectuée avec une précision bien plus grande, par l'emploi d'un densitomètre.

Nous avons pu doser par cette méthode la quantité d'eau qu'une plante est susceptible de perdre par la transpiration foliaire, ainsi que la proportion d'humidité qui peut traverser par diffusion et dissolution les matières plastiques de structures et de compositions différentes.

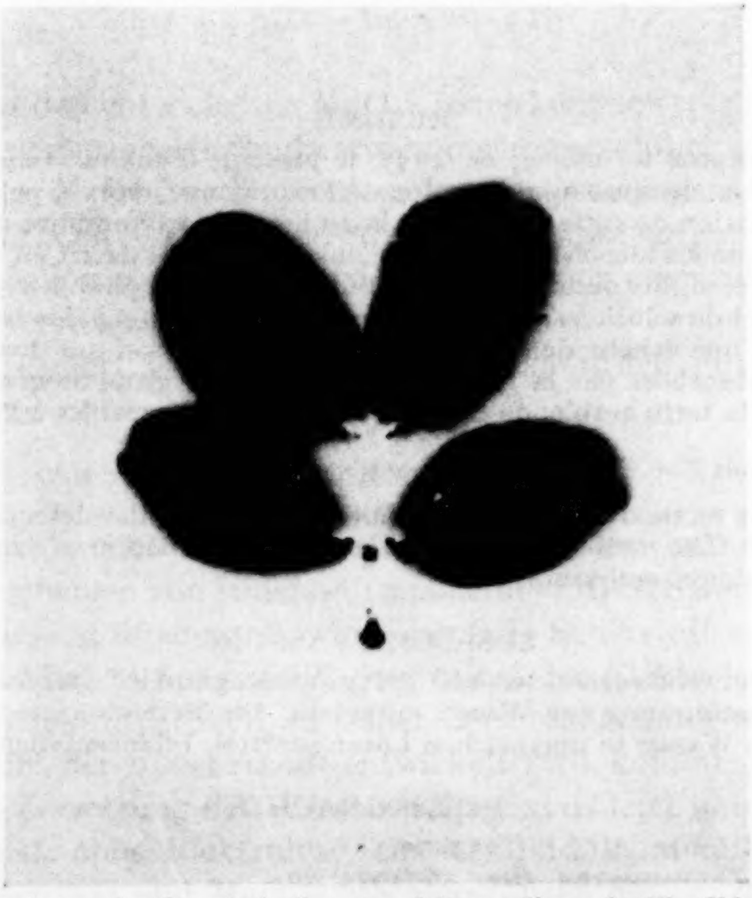

Fig. 6. La transpiration de la face supérieure d'une feuille d'Arachide.

Sans entrer dans les détails de ces analyses, dont les résultats paraîtront ailleurs, nous reproduisons, à titre d'exemples, deux hygrophotographies, dont l'une représente la transpiration de la face supérieure d'une feuille d'Arachide (Fig. 6) et l'autre, la perméabilité de deux échantillons de matières plastiques à l'humidité (Fig. 7) et il suffit de les comparer à l'échelle densitométrique de la figure 5, pour obtenir le résultat analytique cherché.

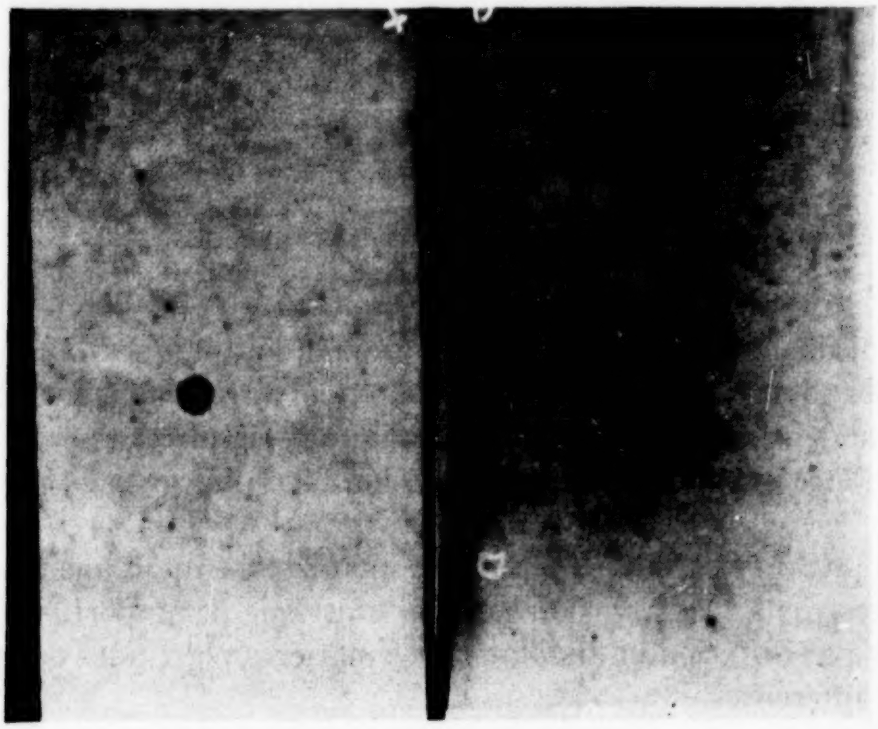

Fig. 7. La perméabilité à l'eau de deux échantillons de matières plastiques.

RÉSUMÉ

L'auteur qui avait exposé ici même, en 1953, le principe d'une nouvelle méthode analytique, dite hygrophotographie, destinée à la détection de l'eau, donne, dans le présent travail, quelques exemples sur l'application de cette méthode à la recherche de l'humidité dans les solvants organiques neutres, tels que les alcools, l'acétone, le dioxane, etc. Il décrit en outre la technique qui permet d'obtenir des résultats quantitatifs par l'étalonnage de la plaque hygrophotographique au moyen de l'eau pure et de solutions aqueuses de bromure de sodium à des concentrations croissantes. On obtient ainsi une échelle densitométrique de comparaison qui donne le moyen de doser les quantités d'eau absorbées par la gélatine de la plaque hygrophotographique au contact des feuilles végétales, de la terre arable, de matières plastiques perméables à l'eau, etc.

SUMMARY

Some applications of a method called "hygrophotography" for the detection and determination of water are described. The method is suitable for the determination of small quantities of water in organic solvents, plants, soil samples, etc.

ZUSAMMENFASSUNG

Es werden einige Anwendungen der als ,,Hygrophotographie" bezeichneten Methode zum Nachweis und der Bestimmung von Wasser mitgeteilt. Die Methode eignet sich zur Bestimmung von geringen Mengen Wasser in organischen Lösungsmittel, Pflanzenteilen, Erdproben usw.

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COULOMETRISCHE PERMANGANATOMETRISCHE BESTIMMUNG VON WASSERSTOFFPEROXYD

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Durch Elektrolyse saurer wässriger Lösungen von Mangansulfat wird an der Anode die Oxydation des Mn^{+2} Ions in MnO_4^- Ion bewirkt. Auf Grund des Studiums der Anodenpotentiale und der anodischen Oxydationsprozesse bei der Elektrolyse schwefelsaurer Lösungen von Mangansulfat haben TUTUNDŽIĆ UND MLADENOVIĆ[1] die Bedingungen für die quantitative anodische elektrolytische Bildung von Permanganationen ermittelt und haben auf dieser Grundlage die coulometrische Permanganatometrie aufgebaut. Anodische Oxydation der Mn^{+2} Ionen zu MnO_4^- Ionen ist quantitativ bei der Elektrolyse wässriger 0.45 bis 0.027 M Lösungen von Mangansulfat und 3.6 N und stärkerer Schwefelsäure. Das Anodenpotential muss positiver als 1.40 V sein und darf den Wert $e_h = 1.7$ V nicht überschreiten. Unter diesen Bedingungen ist die anodische Reaktion

$$Mn^{+2} + 4\,H_2O \rightarrow MnO_4^- + 8\,H^+ + 5\,e$$

quantitativ und mit den entwickelten MnO_4^- Ionen können verschiedene quantitative analytische permanganatometrische Bestimmungen ausgeführt werden.

Bis jetzt sind die Methoden für coulometrische permanganatometrische Mikrobestimmungen von Oxalat-, Ferro- und Arsenitionen ausgearbeitet worden[2,3].

Die coulometrische Permanganatometrie haben wir nun auch zur Mikrobestimmung von Wasserstoffperoxyd angewandt.

In saurer Mitte reagiert Wasserstoffperoxyd, bekanntlich, mit Permanganationen nach der Gleichung

$$5\,H_2O_2 + 2\,MnO_4^- + 6\,H^+ = 5\,O_2 + 2\,Mn^{+2} + 8\,H_2O$$

Bei Zimmertemperatur tritt die Sauerstoffentwicklung auf, während bei niedrigerer Temperatur das Erscheinen von Sauerstoff ausbleibt[4,5]. Durch unmittelbare anodische Oxydation des Wasserstoffperoxyds wird ebenfalls Sauerstoff entwickelt[6,7]. TANATAR[6] und SCHÖNE[7,8] haben festgestellt, dass es bei der Elektrolyse saurer wässriger Lösungen von Wasserstoffperoxyd zu seiner Zersetzung unter der Einwirkung des atomaren Sauerstoffs, der an der Anode entwickelt wird, kommt.

Die katalytische Zersetzung des Wasserstoffperoxyds tritt unter dem Einfluss der Platinelektrode, auch ohne Elektrolyse, ein[6,9,10] und kann auch durch Glas[11,12], Fe^{+2} und Fe^{+3} Ionen[13,14] und MnO_2[15], als Substanzen die bei der coulometrischen

Permanganatometrie von Bedeutung sind, hervorgerufen werden. Mn^{+2} Ion beschleunigt die katalytische Zersetzung des Wasserstoffperoxyds unter dem Einfluss des Glases[12]. Auf Grund des Studiums der Kinetik der Reaktion des Wasserstoffperoxydes mit Kaliumpermanganat nehmen BAILEY UND TAYLOR[16] an, dass Wasserstoffperoxyd die partiell reduzierten Manganionen, wie z.B. MnO_3^- Ionen[17] reoxydiert, was niedrigere Resultate bei der Bestimmung des Wasserstoffperoxyds ergeben könnte.

Bei der coulometrischen permanganatometrischen Bestimmung der Oxalat-, Ferro- und Arsenitionen haben TUTUNDŽIĆ UND MLADENOVIĆ das Ende der Titration mit Hilfe von *o*-Phenanthrolin–Ferro-Komplex, Feroin, festgestellt[1,2]. Das Normaloxydationspotential des Feroins hat den Wert von 1.06 V, während die Farbänderung bei 1.12 V, für pH = 0, eintritt[13,19]. Das Ende der Titration haben TUTUNDŽIĆ UND MLADENOVIĆ bei Bestimmung des Ferroions unmittelbar durch Farbänderung des Indikators festgestellt, während sie bei den coulometrischen permanganatometrischen Titrationen der Oxalat- und Arsenitionen sich der indirekten Endpunktbestimmung, mittels desselben Indikators, bedienten.

VERFAHREN

Bei der Ausarbeitung der coulometrischen permanganatometrischen Methode zur Mikrobestimmung von Wasserstoffperoxyd wurden die direkte, sowie die indirekte Methode der Endpunktbestimmung, angewandt.

Das Oxydationspotential des Wasserstoffperoxyds hat, unter unseren Arbeitsbedingungen, einen Wert bei dem sich das Feroin grösstenteils in seiner Oxydationsform befindet und wenn dem Grundelektrolyten, in dem schon das Feroin in seiner Oxydationsform vorhanden ist, das zu bestimmende Wasserstoffperoxyd zugegeben wird, erscheint die Farbe der Reduktionsform des Indikators nicht mehr, weswegen das Feroin als Indikator zur direkten Endpunktbestimmung nicht geeignet ist.

Daher muss bei der Bestimmung des Wasserstoffperoxyds ein Indikator mit positiverem Normaloxydationspotential verwendet werden. Die Anwendung des 5-Nitro-*o*-Phenanthrolins zur Endpunktbestimmung durch die direkte Methode hat zu sehr zufriedenstellenden Resultaten geführt. Das Normaloxydationspotential dieses Indikators ist positiver als das Normaloxydationspotential des Feroins und beträgt 1.25 V, während die Farbänderung bei 1.31 V, für pH = 0, eintritt[20]. Gibt man dem Grundelektrolyten diesen Indikator zu und oxydiert man ihn nachher durch elektrolytisch erzeugte Permanganationen bis zu der Ferriform und fügt man dem so bereiteten Anolyten das zu bestimmende Wasserstoffperoxyd zu, so bemerkt man, dass schon die ersten zugegebenen Tropfen die rote Farbe der Reduktionsform wieder hervorrufen. Nur im Falle, dass der Grundelektrolyt mehr als 10 *N* Schwefelsäure enthält, erscheint die rote Färbung des vorher oxydierten Indikators nach der Zugabe des Wasserstoffperoxydes nicht mehr wieder und unter diesen Bedingungen kann das Nitro-Feroin für unmittelbare Bestimmung des Endpunktes der Titration nicht angewandt werden. Zahlreiche Bestimmungen haben bewiesen, dass 5-Nitro-*o*-Phenanthrolin als Indikator mit gutem Erfolg für die direkte Endpunktbestimmung bei der coulometrischen permanganatometrischen Titration des Wasserstoffperoxyds angewandt werden kann. Die Indikatorlösung wird auf dieselbe Weise wie die Feroinlösung bereitet, wovon 6–8 Tropfen einer 1 : 3 Lösung (1 Teil 0.025 *M* und 3 Teile Wasser) benutzt werden.

Bei indirekten Endpunktbestimmungen kann mit Erfolg als Indikator ebenfalls 5-Nitro-*o*-Phenanthrolin, sowie auch Feroin verwendet werden.

Das Verfahren, sowie die Apparatur für coulometrische permanganatometrische Mikrotitration des Wasserstoffperoxyds sind dieselben wie diejenigen für die Bestimmung von Oxalat-, Ferro- und Arsenitionen[2]. Die Elektrolyse wird bei konstanter und genau bekannter Stromstärke, ausgeführt. Die Änderungen der Stromstärke, durch Änderung der Leitfähigkeit der Zelle, sowie durch Wärme-Effekt in Aussenwiderständen hervorgerufen, kann leicht kompensiert werden. Anolyt und Katholyt müssen auch für diese Bestimmungen getrennt werden, um die Reduktion der gebildeten Permanganationen an der Kathode zu vermeiden. Der Grundelektrolyt, der als Anolyt, sowie als Katholyt dient und auch den elektrolytischen Schlüssel ausfüllt, enthält meistens eine 0.2 N Lösung von Mangansulfat in 6 bis 7 N Schwefelsäure. Es wurde auch mit verschiedenen Konzentrationen der Schwefelsäure von 3.6 N bis 14 N gearbeitet und festgestellt, dass es beim Arbeiten mit einem Anolyten mit 3.6 N und 4 N Lösung von Schwefelsäure zur Bildung einer MnO_2-Schicht an der Anode kommt, was positive Fehler von 0.3 bis 0.8% verursacht.

Durch diese coulometrische permanganatometrische Methode können sehr leicht und genau 1 bis 5.5 mg Wasserstoffperoxyd in 50 ml des Grundelektrolyten mit Stromstärken von etwa 8 und 10 mA bestimmt werden, wobei in einer Sekunde etwa $1.5 \cdot 10^{-3}$ mg, bzw. $1.8 \cdot 10^{-3}$ mg Wasserstoffperoxyd oxydiert werden. Während der Titration soll die Temperatur des Anolyten von 30° bis 32° eingehalten werden, um die Zersetzung des Wasserstoffperoxydes unter dem Einfluss der erhöhten Temperatur in annehmbaren Grenzen zu halten. Während der Ausführung der Bestimmung wird der Anolyt mechanisch mässig gerührt. Durch Änderung der Elektrodenoberfläche konnte nach Bedarf die Stromdichte variiert werden.

Bei indirekten coulometrischen Analysen mit konstanter Stromstärke muss die angewandte Stromstärke kleiner sein, als der Grenzstrom des Elektrodenprozesses, durch welches das Reagens primär erzeugt wird. Bei der anodischen Oxydation des Mn^{+2} Ions zum MnO_4^- Ion hängt die Grenzstromstärke von der Temperatur, von der Konzentration der Schwefelsäure und des Mangansulfats, sowie vom dessen Verhältnis ab, wobei alle drei Faktoren die Grenzstromstärke erhöhen und hauptsächlich die Konzentration des Mangansulfats, in Abhängigkeit von der zu bestimmenden Wasserstoffperoxydmenge. Die Analysenresultate stimmen mit den theoretischen Betrachtungen überein und zeigen, dass die festgestellten Bedingungen für Indikatoren[21] auch für die coulometrische permanganatometrische Bestimmung des Wasserstoffperoxydes ihre Gültigkeit haben.

Bei der indirekten Methode ist es bei ungenügender Reinheit der Reaktive nötig eine Prätitration auszuführen, während bei der direkten Methode der Endpunktbestimmung die Prätitration der Begleitstoffe mitinbegriffen ist. Beide Methoden, mit gleichzeitiger Prätitration, stellen zu gleicher Zeit ein Verfahren für die Einstellung des Anolyten auf das Potential des Endpunktes der Titration durch Anwendung des Indikators dar, analog der Einstellung des Elektrolyten auf das Potential des Endpunktes der Titration durch Anwendung der potentiometrischen Methode der Endpunktbestimmung[22,23], was man als ein allgemeines Verfahren für die Anwendung der Redox-Indikatoren bei der coulometrischen Titration betrachten kann.

TABELLE I

INDIREKTE COULOMETRISCHE METHODE

Indikator Feroin: $i = 10.40$ mA

Strom-dichte mA/cm²	*Temperatur °C*	*Grundelektrolyt, 50 ml*		*mg H_2O_2*		*Fehler*		*Dauer sec*
		H_2SO_4 N	*$MnSO_4 \cdot 4H_2O$ M*	*Genommen*	*Gefunden*	*mg*	*%*	
0.20	30°	6	0.067	1.143	1.151	0.008	0.7	628.0
				2.285	2.272	—0.014	—0.6	1.238.9
0.45	21–22°	6	0.54	2.794	2.786	—0.008	—0.3	1.520.0
				4.192	4.166	—0.026	—0.6	2.272.6
		6.5	0.13	0.699	0.703	0.004	0.6	383.4
				1.397	1.391	—0.006	—0.4	758.6
				2.794	2.790	—0.004	—0.1	1.521.9
	20° (±1)	7	0.18	1.590	1.579	—0.011	—0.7	861.3
				2.385	2.373	—0.012	—0.5	1.294.5
				3.180	3.164	—0.016	—0.5	1.725.9
	21–22°	14	0.045	1.397	1.407	0.010	0.7	767.3[a]
				1.397	1.403	0.006	0.4	765.1[a]
	30° (±2)	6	0.045	4.219	4.196	—0.023	—0.6	2.288.7
			0.090	4.219	4.209	—0.010	—0.2	2.296.5
			0.36	4.219	4.208	—0.011	—0.3	2.295.7
1.5	20° (±1)	7	0.54	1.590	1.587	—0.003	—0.2	865.9
				1.590	1.595	0.005	0.3	870.0
				2.385	2.382	—0.003	—0.1	1.299.7
				2.703	2.693	—0.010	—0.4	1.689.3
				3.180	3.178	—0.002	—0.1	1.733.5
				3.975	3.969	—0.006	—0.2	2.165.4
	30° (±2)	6	0.36	4.219	4.214	—0.005	—0.1	2.298.6
		8	0.18	4.220	4.207	—0.013	—0.3	2.294.8
			0.27	4.221	4.215	—0.006	—0.1	2.301.4
			0.36	4.220	4.219	—0.001	—0.0	2.301.7
			0.45	4.221	4.209	—0.012	—0.3	2.294.2
			0.36	4.219	4.216	—0.003	0.1	2.299.9
				5.627	5.598	—0.029	—0.5	3.053.6
		10	0.36	4.219	4.224	0.005	0.1	2.304.5

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[a] Indikator Nitro-Feroin

TABELLE II

DIREKTE METHODE

Indikator Nitro-Feroin: $i = 10.40$ mA

Strom-dichte mA/cm²	*Temperatur °C*	*Grundelektrolyt*			*mg H_2O_2*		*Fehler*		*Dauer sec*
		ml	*H_2SO_4 N*	*$MnSO_4 \cdot 4H_2O$ M*	*Genommen*	*Gefunden*	*mg*	*%*	
0.4	30° (±1)	50	6	0.067	1.143	1.141	—0.002	—0.2	622.2
					1.143	1.146	0.003	0.3	625.1
1.5	21–22°	25	7	0.45	1.397	1.404	0.007	0.5	765.8
			7	0.54	1.397	1.386	—0.011	—0.8	756.2
					1.397	1.404	0.007	0.5	765.7
			6	0.54	1.397	1.409	0.012	0.9	768.5
					1.397	1.393	—0.004	—0.3	760.0
			10	0.45	1.590	1.576	—0.014	—0.9	860.0
	30° (±2)	50	8	0.36	4.220	4.218	—0.002	—0.1	2.301.0
					4.220	4.219	—0.001	—0.0	2.301.0

ERGEBNISSE

Einige der erzielten Resultate, unter den schon angegebenen Bedingungen, enthalten Tabellen I und II.

Aus den Tabellen I und II ersieht man, dass die meisten Bestimmungen einen negativen Fehler aufweisen. Ein Grund dafür liegt, unserer Meinung nach, in der Einwirkung des Platins, da wir feststellen konnten, dass es unter unseren Arbeitsbedingungen auch zu katalytischer Zersetzung des Wasserstoffperoxyds an der Anode kommen kann. Deswegen ist es, unserer Erfahrung nach, ratsam mit einer Anode aus Platin, die so klein als möglich ist, und schnell zu arbeiten, auf welche Weise man, wie die Ergebnisse zeigen, sehr gute Resultate erzielen kann.

ZUSAMMENFASSUNG

Es wurde eine coulometrische permanganatometrische Methode zur Mikrobestimmung von Wasserstoffperoxyd entwickelt. Die Endpunktbestimmung wird mit Hilfe des *o*-Phenanthrolin–Ferro-Komplexes und des 5-Nitro-*o*-Phenanthrolin–Ferro-Komplexes als Indikator bewirkt.

Die Resultate bewegen sich in den üblichen Fehlergrenzen der schon ausgeführten coulometrischen permanganatometrischen Mikrobestimmungen, wobei die specifischen Eigenschaften des Wasserstoffperoxyds, sowie seine Unbeständigkeit in Betracht gezogen werden müssen.

SUMMARY

A method has been developed for the quantitative coulometric permanganatometric micro-determination of hydrogen peroxide. The end-point is ascertained by the colour changes of the indicators ferroin, and nitro-ferroin respectively.

RÉSUMÉ

Une méthode coulométrique par permanganatométrie est présentée pour le dosage de l'eau oxygénée à l'échelle micro. La détermination du point final est effectuée à l'aide de ferroïne ou nitro-ferroïne comme indicateur.

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Short Communications

Determination of niobium in the presence of tantalum after extraction with methyl isobutyl ketone

In a recent paper[1] it was shown that germanium extracted from hydrochloric acid solution with methyl isobutyl ketone can be made to react directly in the organic phase with phenylfluorone and then determined spectrophotometrically.

Niobium(V) was found to interfere in this procedure and had to be removed before performing the germanium extraction, but no interference due to the presence of tantalum(V) was observed.

On the basis of these findings it seemed possible that a method for the determination of niobium in the presence of tantalum could be developed.

The efficiency of the extraction was investigated by using solutions containing sulfuric + tartaric acids, which were made 7.5 *N* in hydrochloric acid. 1.0 ml of the aqueous hydrochloric solution was extracted with 1.0 ml of methyl isobutyl ketone, the content of niobium being varied from 10 to 200 μg. In every case 90% of the niobium was extracted in a single operation.

The extracted niobium reacts instantaneously in the organic phase with an alcoholic solution of phenylfluorone, giving a stable colored solution. Experiments performed according to the procedure given below showed that at the wave length of maximum absorption, 502 mμ, Beer's law is obeyed in the range studied, which was 0.2 to 2.0 μg Nb/ml; a Ringbom plot indicated the optimum concentration range to be 0.5 to 1.6 μg Nb/ml (final dilution). Spectrophotometric readings were found to be reproducible within 24 h after exposure to ordinary light at room temperature.

It was found that tantalum was not extracted by the treatment outlined above. Extraction experiments were carried out with pure tantalum solutions containing 10 and 1000 μg Ta/ml and the element was always quantitatively recovered in the aqueous phase. Furthermore, evidence was obtained that tantalum does not react with phenylfluorone in organic solution under the conditions of the procedure studied.

Experiments for the determination of niobium in the presence of tantalum were run with solutions containing 10 μg Nb and either 10, 200, 500 or 1000 μg Ta. Results were in perfect agreement with those obtained with the same concentration of niobium in absence of tantalum and no interference was observed in any region of the spectrum of the colored solution. It was also found that tantalum can be quantitatively extracted from the remaining aqueous phase with methyl isobutyl ketone after addition of sufficient hydrofluoric acid to make the solution about 2% in HF. Thus if necessary, tantalum can be determined, after separation of niobium, by the procedure given by LUKE[2].

The procedure reported in this communication is intended for application to the determination of niobium in mixtures of niobium and tantalum pentoxides, which are fused in the usual manner in a platinum crucible with excess potassium pyrosulfate. The melt is brought into solution with the aid of a mixture of 10% sulfuric and 10% tartaric acids.

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Procedure

Place in a test tube with a ground glass stopper 1.0 ml of the tartaric–sulfuric solution, which should preferably contain 5 to 15 μg of niobium. Add 2.0 ml of concentrated hydrochloric acid ($d = 1.18$) and extract successively with one 1-ml and two 0.7-ml portions of methyl isobutyl ketone, shaking vigorously each time. Collect the extracts in a 10-ml volumetric flask. Add 3.0 ml of an alcoholic solution of phenylfluorone (0.02% phenylfluorone in a mixture of 95 ml ethyl alcohol and 5 ml H_2SO_4 (1 : 6))[1] and fill up to the mark with ethyl alcohol. Read the transmittance at 502 mμ against a blank.

In the course of this study a Beckman DU spectrophotometer and 1-cm Corex cells with ground glass stoppers were used. The same extraction technique previously reported[1] was employed.

A detailed paper on this subject including an investigation of the influence of foreign ions will be published later.

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A simple and rapid determination of small amounts of adenine

The determination of small quantities of adenine usually demands complicated analytical techniques, such as spectrophotometry[1], polarography[2], colorimetry after bromination[3] etc. We have developed a new method for the determination of small

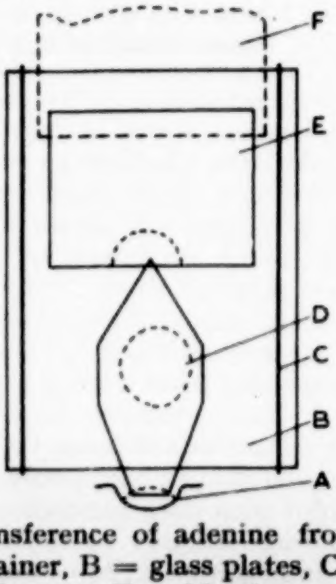

Fig. 1. Arrangement for direct transference of adenine from a chromatographic spot to the impregnated paper. A = water container, B = glass plates, C = plastic, D = spot, E = impregnated paper, F = blotting paper.

quantities of adenine (in the range 3–10 μg). The method is based on the measurement of the size of the spots formed on paper impregnated with silver arsenate when an aqueous solution of adenine is spotted on the paper and the spot is developed. The size of spot is proportional to the amount of adenine added.

The impregnated paper was prepared by immersing a strip of Whatman No. 1 chromatographic paper in an aqueous 0.1% silver nitrate solution, and after drying, in an aqueous 0.2% potassium arsenate solution; the method of impregnation has already been described in detail[4]. The paper impregnated with silver arsenate is very sensitive to light, and must be kept in the dark.

The aqueous solution of adenine can be placed on the impregnated paper directly from a micropipette or microextractor[5], or by means of the arrangement described previously for the analysis of phosphorus[6]. When adenine is to be estimated directly on a chromatogram, the elution process can be omitted; the adenine can be transferred directly from the spot on to the impregnated paper as illustrated in Fig. 1.

After the test solution has been placed on impregnated paper, the spot obtained must be diluted with 0.2–0.3 ml of distilled water.

The spot is then made visible by immersion for 1–2 min in photographic developer Ilford 1D2[7]. A white fleck of the complex of adenine with silver appears on the black background. The white spot is fixed by acid photographic solution. The spot is stable in the dark and its area can be measured by some suitable method[8]. The size of the spot is then compared with the control series on a suitable diagram. The analysis must be done in the dark.

The error in the results is about ± 5%.

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BOOK REVIEWS

Qualitative analysis and analytical chemical separations, by P. W. West and M. M. Vick. 2nd Ed., The Macmillan Company, New York 1959, Pp. xv + 302, $ 4.5.

The authors of this book have presented a new approach to the teaching of qualitative inorganic analysis in order that students may better derive the maximum benefit from their work in this field. The basis of the new approach is a non-sulphide scheme of analysis which, it is claimed, offers advantages, both in theory and in practice, over the classical hydrogen sulphide scheme.

The contents of the book are divided into three parts: *Experimental, Fundamental Theory* and *The Metals*.

Part I, *Experimental* (84 pp.), is devoted mainly to the actual cation separation scheme. The latter involves the successive precipitation, from a single portion of sample solution, of a Chloride Group (Hg_2^{+2} and Ag^+), a Basic Benzoate Group (Sn^{+4}, Bi^{+3}, Sb^{+3}, Ge^{+3}, Al^{+3} and Cr^{+3}), a Fluoride Group (Pb^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2} and Ca^{+2}), a Hydroxide or Non-amphoteric Group (Mn^{+2}, Fe^{+2}, Hg^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2} and Cd^{+2}), leaving only an Amphoteric Group (Sn^{+2}, As^{+3} and Zn^{+2}) in the final solution. Examination is made for a Soluble Group (Na^+, K^+ and NH_4^+) on a second portion of the sample solution. The subject matter is arranged so that the reason behind every operation is to be derived from the carrying out of preliminary exercises, while discussions and explanations follow in the portion of the text dealing with the running of an unknown sample.

The method adopted for analysis of the anions, inherently more difficult than for analysis of the cations, contains nothing particularly new. It is based on such classical procedures as precipitation of anions with Ba^{+2}, Ca^{+2} and Ag^+ in solutions of varying acidity. These results are then considered in conjunction with those derived from preliminary tests, such as gases evolved upon acidification, oxidizing and reducing properties.

Peculiarly, there appears to be no mention of how much sample to take nor of how to prepare a solution of the sample for cation analysis. Directions given in the separation scheme seem to indicate a semi-micro scale of working. Advantages to be gained by working at less than macro levels might usefully be mentioned. The remarks on apparatus and technique (2½ pp.) are, in the reviewer's opinion, much to condensed. They could profitably be expanded and preferably illustrated. It is, however, pleasing to see the need to avoid contamination of reagent solutions (p. 8) and the advisability of carrying out both *control* and *blank* tests (p. 13) receive more emphasis than usual.

The authors have found it "not practical to delay the beginning of laboratory work until the student has mastered all of the theory which is required for the proper understanding of all of the procedures". *Fundamental Theory* (124 pp.) is, therefore, placed in Part II after the *Experimental* in Part I. Many people would doubtless still prefer the alternative arrangement. Close inspection of chapters comprising Part II confirms the authors' view that presentation of theory is much easier when associated with their non-sulphide scheme than when combined with classical hydrogen sulphide-based analysis. The inclusion of a series of questions and problems at the end of nearly every chapter is a useful feature.

Part III, *The Metals* (64 pp.) is sub-divided into *Metals and Metallurgy* and into *Reactions of the Metals and Metal Ions*. The material on metallurgy and chemistry of the metals appears for the first time in the second edition, having been added to provide a text suitable also for requirements of general chemistry. The need to make this change is greatly regretted by the reviewer for, in his opinion, the real value of the book lies rather in its attempt to present a new approach to qualitative inorganic analysis than in its expansion into a "several purpose" text. Only the summarised reactions of the various metal ions are particularly relevant to the teaching of analysis.

Two interesting additions have been made to the *Appendix* (21 pp.) short sections on spot test procedures and on mathematical operations. The spot tests should provide a valuable means of double-checking results obtained by the systematic scheme of analysis.

Non-sulphide approaches to qualitative analysis have previously been introduced, but none has stood the test of time in comparison with the classical hydrogen sulphide scheme. It is, therefore, significant that, in student hands for over four years at more than sixty institutions in the United States, the present scheme has proved itself capable of getting results comparable or superior to the classical scheme. This is the ultimate proof of the worth of any scheme. Since the book is specially designed for use in a United States teaching institution, its adoption can confidently be expected to become more widespread in that country.

Elsewhere, particularly where the classical hydrogen sulphide scheme still enjoys an almost complete ascendancy, it is more difficult to visualise the non-sulphide approach gaining rapid recognition. Such problems as acid and sulphide fumes have been largely eliminated by the universal scaling down of the hydrogen sulphide scheme from a macro to a semi-micro level of operation. At the same time much sharper group separations are possible. Further, at least one group of workers (*Mikrochim. Acta*, 12 (1956) 1842) is actively concerned with general improvement of the hydrogen sulphide scheme. The many teachers not seeking a change from the use of hydrogen sulphide would do well, however, to read this book carefully. The new ideas it puts forward present a serious challenge to the supremacy so long enjoyed by the classical scheme of qualitative inorganic analysis.

Finally, the title of the book is somewhat misleading. The contents might be better described by "*Qualitative Inorganic Analysis. A New Approach*".

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Anal. Chim. Acta, 22 (1960) 299–300

Continuous Analysis of Chemical Process Systems, by SIDNEY SIGGIA, John Wiley and Sons, Inc., New York 1959, Pp. XIII 381, $ 8.50.

In industry today, continuous analysis of chemical processes is rapidly gaining importance. Such analyses are necessarily instrumental, frequently automatic and are sometimes geared to activate control circuits which automatically make adjustments to the chemical system being analysed. However much one may deplore increasing mechanisation of the analysts art and the replacement of the analyst and plant control chemist by automatic analytical-cum-reaction-control instruments, one must recognize that the situation does now exist.

This book represents the first monograph on continuous analysis of chemical process systems. The author has been faced with the paucity of published papers and has had to rely very largely on technical data and, to a lesser extent, advertising literature supplied by the instrument manufacturers. The material is therefore classified alphabetically according to manufacturer's name within sixteen chapter headings which deal with the physical property being determined *e.g.* refractive index, U.V. absorption, mass spectrometry, etc. Five other chapters are devoted to the measurement of moisture, oxygen, carbon dioxide, combustibles and water hardness; the final two chapters are concerned with automatic chemical analysis and instruments in the research or development stage.

The overall impression gained from a survey of this book is that it will be invaluable to those who desire to select and install such instrumentation; nowhere else is such a compilation available. It does not constitute a text-book of instrumental analysis and consequently its use to the analytical chemist is very largely restricted to interest-value. The coverage is very wide and must be virtually complete. For such a restricted specialist reading public, the cost is extremely moderate.

T. S. WEST (Birmingham)

Anal. Chim. Acta, 22 (1960) 300

Communication

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
ANALYTICAL CHEMISTRY SECTION

During the XXth Conference of the I.U.P.A.C. which was held in Munich in August, 1959, the Committee of the above Section discussed certain points of confusion in the literature. Recommendations were made as follows:

1. *Notation of indicators in titrimetric analysis.* Many dyestuffs have been recommended as indicators in chelatometric and redox titrations and a host of trivial names often exists for the same compound. Examples can be found in the literature of a compound having been recommended as a new indicator because it has a different name when the compound has in fact been in use for years under a different name.

To avoid future confusion and embarrassment of authors and editors, the Committee recommends that when a dyestuff is proposed as an indicator in any type of titration, and particularly when it is claimed as new, the British Colour Index or Schultz Number be quoted along with the trivial name.

2. *Terminology of complexing agents.* Because of the existing confusion regarding terminology in the use of complexing agents as titrants, the committee tentatively recommends the use of the following terms until such time further action is taken.

a. The group of polyamino-polycarboxylic acids which form *anionic* complexes shall be termed "complexans".

b. Titration processes in which any type of complexing titrant is used shall be termed "complexometric".

c. Those complexometric titrations which involve titration with a chelating agent shall be termed "chelatometric titrations" and represent a special type of complexometric titration.

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SEPARATION AND GRAVIMETRIC DETERMINATION OF NIOBIUM, TANTALUM AND TITANIUM BY PRECIPITATION WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

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INTRODUCTION

N-Benzoyl-N-phenylhydroxylamine, a derivative of cupferron, was originally synthesized by BAMBERGER[1]. The reagent was used by SHOME[2] for the gravimetric determination of aluminium, copper, iron and titanium, and for the colorimetric determination of vanadium. It was recommended by MOSHIER AND SCHWARBERG[3] for the gravimetric determination of tantalum in the presence of niobium, titanium and zirconium. MAJUMDAR AND MUKHERJEE[4,5] used it for the separation and determination of niobium and tantalum.

MOSHIER AND SCHWARBERG separated tantalum by two or three precipitations at pH 1, while niobium and titanium were kept in solution as the fluoride complexes. A procedure for further separation of niobium and titanium was not given by these authors.

MAJUMDAR AND MUKHERJEE precipitated niobium from a tartrate solution at a pH of 3.5–6.5. Tantalum remained in solution and was precipitated by decreasing the pH to below 1.5. Several of the more common elements were kept in solution by means of EDTA* and tartaric acid. Interfering ions were titanium, zirconium, vanadate and molybdate.

The interference caused by titanium reduces considerably the possible application of the reagent in the analysis of niobium- and tantalum-bearing ores and minerals. In these materials the earth acids are usually accompanied by considerable amounts of titanium. The value of N-benzoyl-N-phenylhydroxylamine as an analytical reagent would be greatly increased if it also could be applied in the presence of titanium.

The present paper describes a method for the separation and gravimetric determination of niobium, tantalum and titanium by precipitation with N-benzoyl-N-phenylhydroxylamine. Titanium is kept in solution with EDTA and hydrogen peroxide while the earth acids are precipitated together in 1 *N* sulphuric acid. Niobium and tantalum are then separated and determined by a modification of the method of MAJUMDAR AND MUKHERJEE[4]. After destruction of the complexing agents, titanium is also determined by precipitation with N-benzoyl-N-phenylhydroxylamine.

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* Ethylenediaminetetraacetic acid, disodium salt.

EXPERIMENTAL DATA

Reagents

For the preparation of standard solutions of niobium, tantalum and titanium, known amounts of the pure metals were weighed out. Solutions of these metals tend to hydrolyse on standing; freshly prepared, clear solutions should therefore be used. In addition to these three solutions, combined standard solutions containing two or three of the components were also prepared.

N-Benzoyl-N-phenylhydroxylamine (L. Light & Co.) and other chemicals were of reagent grade quality. A 10% solution of N-benzoyl-N-phenylhydroxylamine in ethanol was used for the precipitations.

Determination of pH

The pH of the solutions was adjusted by means of pH paper indicating pH with an accuracy of ±0.2 units.

Complexing agents for titanium

As mentioned above, the earth acids were precipitated together in 1 *N* sulphuric acid while titanium was complexed and kept in solution. Several complexing agents for titanium were tested. Among those tried unsuccessfully were EDTA, ascorbic acid, hydrogen peroxide, triethanolamine and tiron (catechol-3,5-disulphonic acid).

However, the stability of the titanium–EDTA complex may be increased by adding hydrogen peroxide. WILKINS[6] recommended peroxide to inhibit the precipitation of hydrous oxide from titanium–EDTA solutions; he suggested that one or more peroxide molecules are picked up by the titanium–EDTA complex, displacing hydroxy or oxygen ions. That the stability of this complex is increased by the addition of peroxide was demonstrated by the fact that titanium was precipitated with N-benzoyl-N-phenylhydroxylamine when the solution (1 *N* sulphuric acid) contained only EDTA, while no precipitation took place from a similar solution containing both EDTA and hydrogen peroxide.

All the titanium could not be kept in solution during the precipitation of niobium and tantalum. About 10% of the amount present was coprecipitated with the earth acids, and a double precipitation is therefore recommended. During the subsequent precipitations of niobium and tantalum, the small amount of titanium remaining with the earth acids went into solution and was finally recovered in the washings.

Procedure for the separation and determination of niobium, tantalum and titanium

(A satisfactory, preliminary separation of the three elements from other elements present in the materials to be analyzed is obtained by a double precipitation with N-benzoyl-N-phenylhydroxylamine at a pH below 1. Niobium, tantalum and titanium are thus quantitatively separated from several other elements which are kept in solution by complex formation with EDTA and tartaric acid.)

A sample (0.2–0.3 g) of the three metals (as oxides) is fused with 2–3 g of potassium pyrosulphate. The melt is dissolved by heating with 30–40 ml of 30% tartaric acid solution containing 2 ml of concentrated sulphuric acid. The resulting solution is transferred to a beaker (800-ml capacity) and diluted to about 300 ml with 2% tartaric acid solution. Sufficient sulphuric acid (1 : 1) is added carefully to make the solution 1 *N* in sulphuric acid. The solution is heated to about 60° on the boiling water bath and then removed from the bath; 1 g of EDTA and 1 ml of 30% hydrogen peroxide solution are added to complex titanium, followed by 30 ml of 10% N-benzoyl-N-phenylhydroxylamine solution added dropwise with stirring. The solution is again placed on the boiling water bath for 45 min at 60° to coagulate the precipitate. Macerated filter paper is added* and the solution is cooled to room temperature. It is then cooled to about 5° in a refrigerator. The yellow precipitate is collected on a loose-textured filter paper and is washed free of sulphate ions with a hot wash solution prepared by dissolving 1 g of N-benzoyl-N-phenylhydroxylamine, 1 g of EDTA and 1 ml of 30% hydrogen peroxide solution in 1 l of distilled water. The washings are reserved for the determination of titanium. The filter is transferred to a porcelain crucible, and the precipitate is dried, charred and ignited at about 600° in an electric furnace.

The oxides are again brought into solution by fusion with potassium pyrosulphate, and niobium and tantalum are reprecipitated with N-benzoyl-N-phenylhydroxylamine, 0.5 g of EDTA and 0.5 ml of 30% hydrogen peroxide solution being added to complex the remaining titanium. The precipitation is done as described above. The washings are reserved for the determination of titanium. The ignited residue contains all the niobium and tantalum and a small amount of titanium. In the subsequent precipitations of niobium at pH 4.5–5.0 and of tantalum at pH about 1, coprecipitated titanium goes into solution and is recovered in the washings. When tantalum is precipitated, EDTA and hydrogen peroxide are again added to keep titanium in solution. EDTA and hydrogen peroxide should not be present during the precipitation of niobium because of the risk of incomplete precipitation.

The further procedure for the separation and determination of niobium and tantalum is as follows. The oxides of the earth acids are decomposed with potassium pyrosulphate and the melt is dissolved by heating with 30–40 ml of 30% tartaric acid solution containing 2 ml of concentrated sulphuric acid. The solution is transferred to a beaker and diluted to about 300 ml with 2% tartaric acid solution. 20 ml of 10% ammonium acetate solution are added so that a buffer action is obtained when ammonia is added. Diluted ammonia solution is added carefully while stirring until the pH is 4.5–5.0. The solution is then heated on the water bath to about 90° and 30 ml of 10% N-benzoyl-N-phenylhydroxylamine solution are added slowly with stirring. The solution is left on the water bath for 30–45 min and is stirred occasionally. Macerated filter paper is added, the beaker is removed from the water bath and cooled to room temperature. The precipitate is filtered on a loose-textured filter paper and washed free of sulphate ions with a hot 0.1% solution of N-benzoyl-N-phenylhydroxylamine in distilled water. It is then transferred to a previously weighed porcelain crucible, dried, charred and ignited to niobium pentoxide at about 900°.

To the washings are added 0.5 g of EDTA and 0.5 ml of 30% hydrogen peroxide solution. The solution is heated on the water bath to about 60° and 1 : 1 sulphuric acid is added until the pH is about 1. Tantalum is precipitated by adding 20 ml of 10% N-benzoyl-N-phenylhydroxylamine solution dropwise while stirring. The solution is left on the water bath for about an hour at 60°. Macerated filter paper is added, and the tantalum precipitate is treated as described in the preceding paragraph for the niobium precipitate.

The washings from the precipitation of tantalum are combined with all previous washings containing titanium, and the resulting solution is evaporated on the boiling water bath. Fuming nitric acid is added to destroy organic matter and excess is removed by heating on the hot plate to copious white fumes of sulphuric acid. The final, clear solution is diluted with distilled water to give a 5% solution of sulphuric acid. The solution is heated on the boiling water bath, macerated filter paper is added*, and titanium is precipitated by adding, while stirring, a 10% solution of N-benzoyl-N-phenylhydroxylamine. The solution is left on the water bath for 45–60 min and is stirred occasionally. It is cooled to room temperature and then to about 5° in a refrigerator. The precipitate is filtered, washed and ignited as in the case of niobium and is finally weighed as titanium dioxide.

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* Marcerated filter paper may also be added before the addition of precipitating agent.

Notes

The amounts of N-benzoyl-N-phenylhydroxylamine added during the different precipitations of niobium, tantalum and titanium were 8–10 times the weight of metal(s) present.

Niobium should be precipitated at a pH of 4.5–5.0. When the pH was 5–6, as prescribed by MAJUMDAR AND MUKHERJEE[6], the coagulation of the precipitate was less satisfactory. The risk of formation of hydrous oxide is also reduced at the lower pH.

The precipitations described above were all carried out in the presence of high concentrations of salts, and sulphate ions were especially liable to be carried down. The precipitates should therefore be thoroughly washed on the filter. In addition to this washing, it is also recommended that the precipitate be transferred to a beaker containing hot wash solution and kept in suspension for some time by vigorous stirring.

In the analysis of complex materials, small amounts of iron and other constituents tend to coprecipitate in the preliminary separations of niobium, tantalum and titanium. During the subsequent separations, the contaminants dissolve and may be recovered in the filtrate after the precipitation of titanium. This filtrate should therefore be reserved for the determination of other constituents.

Analysis of standard solutions

The procedure described above was tested in the analysis of solutions containing known amounts of niobium, tantalum and titanium (Table I). It can be seen that the results for titanium are somewhat high, probably because of residual amounts of sulphate.

TABLE I

SEPARATION AND DETERMINATION OF NIOBIUM, TANTALUM AND TITANIUM WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

mg Nb_2O_5 taken	mg Ta_2O_5 taken	mg Nb_2O_5 + mg Ta_2O_5 taken	mg TiO_2 taken	mg Nb_2O_5 found	mg Ta_2O_5 found	mg Nb_2O_5 + mg Ta_2O_5 found	mg TiO_2 found
143.4	55.2	—	none	143.4	54.2	—	—
143.4	55.2	—	none	142.4	54.6	—	—
—	—	204.1	133.4	—	—	204.3	134.8
—	—	204.1	133.4	—	—	204.6	133.4
—	—	204.1	133.4	—	—	204.0	134.4
—	—	204.1	133.4	—	—	203.2	135.9

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* The addition of macerated filter paper at this stage prevents the precipitate from sticking to the walls of the beaker.

SUMMARY

A method is described for the separation and gravimetric determination of niobium, tantalum and titanium by precipitation with N-benzoyl-N-phenylhydroxylamine. Titanium is kept in solution with EDTA and hydrogen peroxide, and the earth acids are precipitated in 1 *N* sulphuric acid. Niobium and tantalum are separated and determined by a modification of the method of MAJUMDAR AND MUKHERJEE. All three metals are finally precipitated with N-benzoyl-N-phenylhydroxylamine. In the analysis of complex materials niobium, tantalum and titanium are separated from other constituents by a double precipitation with N-benzoyl-N-phenylhydroxylamine in the presence of EDTA and tartaric acid.

RÉSUMÉ

Une méthode est décrite pour la séparation et le dosage gravimétrique du niobium, du tantale et du titane par précipitation au moyen de la benzoylphénylhydroxylamine. Le titane peut-être maintenu en solution par l'EDTA en présence de peroxyde d'hydrogène. Le niobium et le tantale sont dosés par la méthode proposée par MAJUMDAR ET MUKHERJEE. Le titane est également dosé par le même réactif.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Trennung und gravimetrischen Bestimmung von Niob, Tantal und Titan durch Fällung mit Benzoylphenylhydroxylamin. Titan kann durch EDTA in Gegenwart von Wasserstoffperoxyd in Lösung gehalten werden. Niob und Tantal werden nach der von MAJUMDAR UND MUKHERJEE vorgeschlagenen Methode getrennt und bestimmt. Titan wird ebenfalls durch Fällung mit dem gleichen Reagenz bestimmt.

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Note added in proof

The procedure described in the present paper has been applied recently with satisfactory results in the complete analyses of Blomstrandine and Euxenite, two complex minerals containing essentially niobium, titanium, tantalum, uranium, thorium and yttria earths, as well as a series of minor and trace constituents.

In these analyses the use of hydrofluoric acid as decomposing agent for the minerals and for the oxides of niobium, tantalum and titanium was tried and was found to offer advantages compared with the use of potassium pyrosulphate. The coprecipitation of sulphate was considerably lowered, and in addition a quantitative separation of insoluble rare earth and alkaline earth fluorides from the soluble fluorides of earth acids and titanium was obtained. At the same time quadrivalent uranium was separated from sexivalent uranium. It was also possible to replace the initial double precipitation of niobium, tantalum and titanium (in the presence of EDTA and tartaric acid) by a single precipitation.

The analytical data obtained with the two decomposition methods compared favourably, but the method of attack by hydrofluoric acid seems to offer advantages in the analyses of minerals soluble in this acid.

SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

III. *o*-AMINOPHENOL-*p*-SULPHONIC ACID AS A REAGENT

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In previous papers[1,2] we have discussed the spectrophotometric determinations of osmium present in different valence states by anthranilic and sulphanilic acids. In this paper the use of *o*-aminophenol-*p*-sulphonic acid as a new colorimetric reagent for osmium is described.

o-Aminophenol-*p*-sulphonic acid is a highly sensitive reagent which on reaction with osmium(VI) and (VIII) for 30 min at pH 2.5–4 and at room temperature (34°) gives an intense dark-brown colour with an absorption maximum at 440 mμ. The reagent has no action on tetra-, tri- and bivalent osmium.

EXPERIMENTAL

Apparatus

The optical density of solutions in quartz cells of 1-cm thickness was measured by a Hilger Uvispek Spectrophotometer and the pH was determined by a Cambridge pH meter.

Standard solutions and buffer

Standard solutions of osmium tetroxide and osmate (OsO_4^{-2}), solutions of other ions and the buffer were prepared as reported previously[1,2].

Reagent solution

o-Aminophenol-*p*-sulphonic acid (B.D.H.) was crystallised from water and an aqueous 1% solution of the sodium salt of the reagent was prepared.

Absorbance curves

For absorption studies, solutions were prepared by adding osmate (OsO_4^{-2}) or osmium tetroxide to the reagent solution in a 25-ml flask. The solution was made up to volume with sodium acetate–acetic acid buffer and allowed to stand for 30 min at room temperature. On plotting the optical density of the solutions, as measured against a reagent blank prepared similarly, the region of maximum absorption always occurred at 440 mμ, whether the osmium was in the octavalent or hexavalent state (*cf.* Fig. 1).

Effect of pH, reagent and time

Solutions containing fixed amounts of reagent and osmium were taken in 25-ml flasks and, after adjustment of their pH to different values, were made up to 25 ml with water for the optical density measurements. pH values between 3.42 and 5.9 were obtained with sodium acetate–acetic acid buffers and lower or higher pH values by the addition of sulphuric acid or of sodium hydroxide. The optical density increases with increasing pH from 1 to 2.5, remains constant from pH 2.5 to 4.0 and gives low values above pH 4.0. The pH range 2.5 to 4 was found suitable for all subsequent measurements.

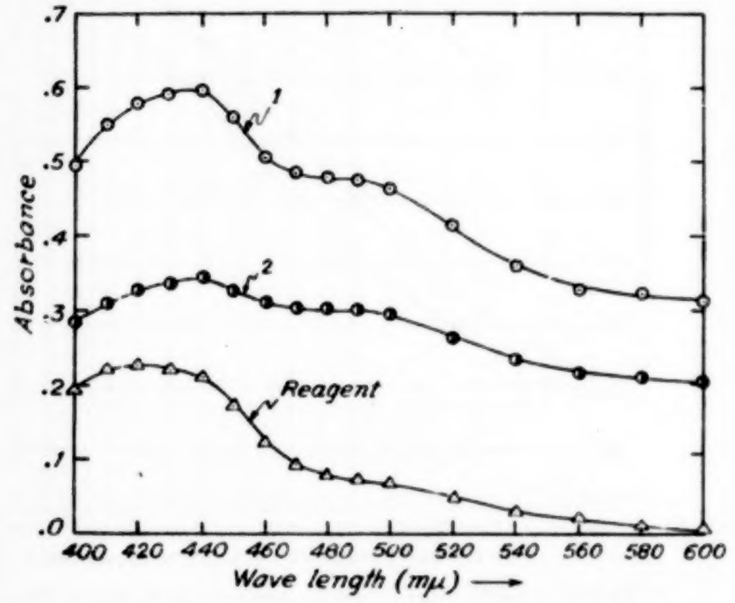

Fig. 1. Absorption curves of *o*-aminophenol-*p*-sulphonic acid (sodium salt) and its osmium complex at pH 3.4. Curve 1 6 p.p.m. osmium(VIII) + 5 ml of 1% reagent. Curve 2. 4 p.p.m. osmium(VI) + 5 ml of 1% reagent.

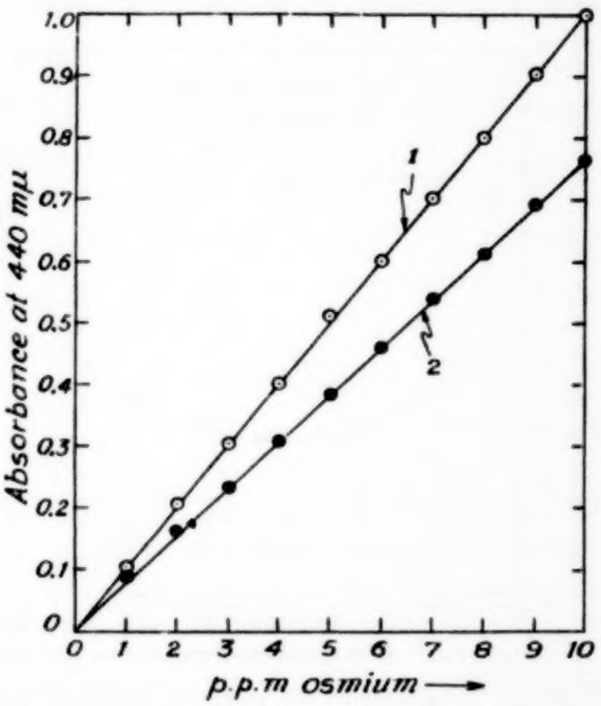

Fig. 2. Beer's law plots for (1) osmium(VIII) and (2) osmium(VI); pH 3.4.

3 ml of the reagent was sufficient for full development of colour with 1 to 10 p.p.m. of osmium. Addition of more reagent did not alter the intensity of the colour. The colour developed immediately but did not remain constant until 30 min had elapsed at room temperature. Even overnight standing had no influence on the colour system.

Beer's law, optimum range and accuracy

Beer's law is obeyed for 1 to 10 p.p.m. of both osmium(VI) and osmium(VIII) (Fig. 2). Measurements were carried out at pH 3.42 against a reagent blank.

As in the previous case[1], the percent relative error per 1% photometric error was plotted against transmittancy to show how the analysis error varied with transmittancy (Fig. 3). Again plotting the % absorbancy at 440 mμ against log concentration (Fig. 4) shows that the optimum concentration range for both osmium(VI) and (VIII) is from 2 to 8 p.p.m. and for this range the % relative errors per 1% absolute photometric error are 3.1 and 2.98 for osmium(VI) and (VIII), respectively. This difference in the relative error is not due to any inherent defect in the method. Since alcohol, which is used to reduce the osmium(VIII) to osmium(VI), lowers the optical density of the colour system (as is evident from the sensitivity and molar extinction coefficient values given below as well from the curves in Figs. 1, 2 and 4) the percent relative error is higher with osmium(VI).

Sensitivity and molar extinction coefficient

SANDELL's spectrophotometric sensitivities, as calculated from Beer's law curves, were found to be 0.012 μg/cm^2 for osmium(VI) and 0.01 μg/cm^2 for osmium(VIII). The molecular extinction coefficients were 15691.5 and 19495.5 for osmium(VI) and (VIII), respectively.

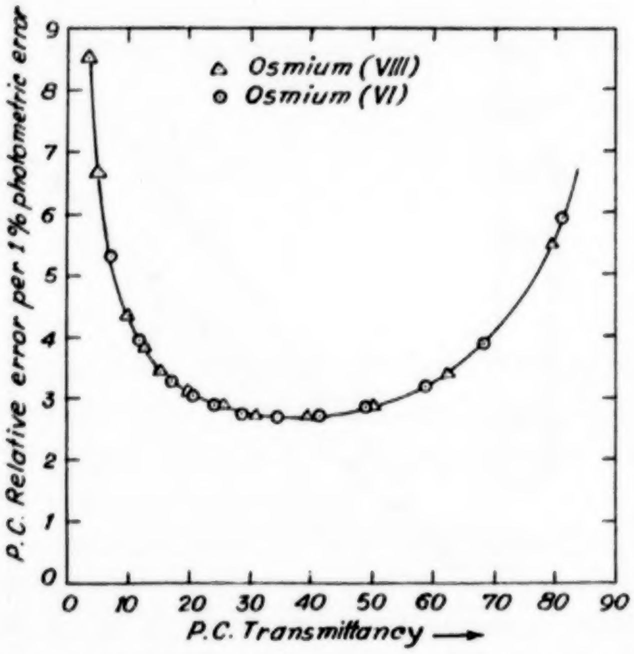

Fig. 3. Evaluation of percent relative error ($dc/c \times 100$) relative to 1% absolute photometric error.

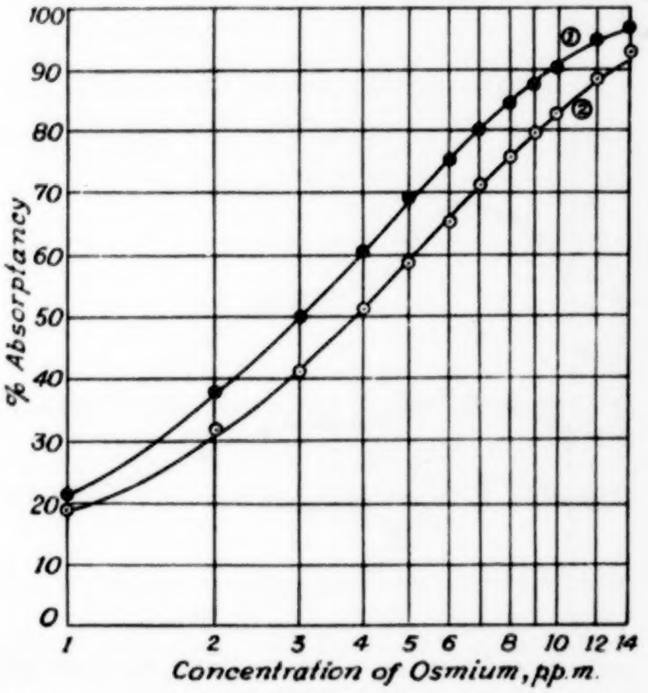

Fig. 4. Calibration curves for (1) osmium(VIII) and (2) osmium(VI) at 440 mμ.

Effect of foreign ions

Osmium(VI) can be determined only in the presence of moderate amounts of Pd^{+2}, Ir^{+4}, WO_4^{-2}, Cr^{+3}, Zn^{+2}, Zr^{+4}, Mg^{+2}, Ba^{+2} and Sr^{+2}. Ions such as Ru^{+3}, Rh^{+3}, UO_2^{+2}, Cu^{+2}, Hg^{+2}, As^{+3}, Bi^{+3}, Fe^{+3}, Al^{+3}, Co^{+2}, Ni^{+2}, Mn^{+2} and Ca^{+2} interfere even at a 1:1 ratio.

Nature of the complex in solution

The Job[5], molar ratio[6] and slope ratio[7] methods confirmed that osmium(VI) forms a 1:2 complex with the reagent.

For these methods, one drop of 6 *M* sulphuric acid was added to the mixed solution of osmium(VI) and the reagent. On the development of the colour the volume of each solution was made up to 25 ml with sodium acetate–acetic acid buffer of pH 3.42. For the slope ratio method, the first series of solutions contained a large excess of the reagent (5 ml of $0.223 \cdot 10^{-3}$ *M*) and varying amounts of osmium(VI) and in the second series the concentrations of osmium(VI) and the reagent were reversed. The optical densities of all the solutions were measured after an hour. The results are graphically represented in Figs. 5, 6 and 7.

With the molar ratio method, a sharp break was found to occur at the osmium(VIII) to reagent ratio of 1:3 (*cf.* Fig. 6). This ratio can be explained by assuming that one molecule of the reagent is oxidised by osmium tetroxide and then a 1:2

complex formation takes place between the reduced osmium(VI) and the unoxidised excess of reagent. That osmium tetroxide and osmate (OsO_4^{-2}) yield the same complex in solution is obvious from their identical colour reaction, tolerance to pH, region of absorption maximum and adherence to Beer's law.

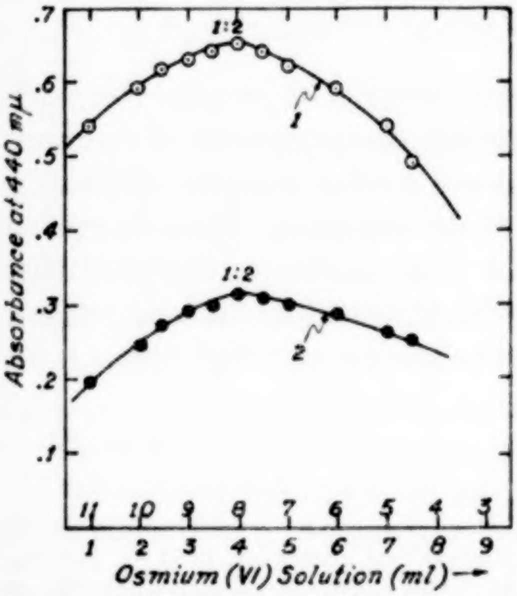

Fig. 5. Determination of the ratio of reagent to osmium(VI) by Job's method. Curve 1. Concentration of osmium(VI) = concentration of *o*-aminophenol-*p*-sulphonic acid (sodium salt) = $0.4325 \cdot 10^{-3}$ *M*; Curve 2. Concentration of osmium(VI) = concentration of *o*-aminophenol-*p*-sulphonic acid (sodium salt) = $0.223 \cdot 10^{-3}$ *M*. Total volume in each case 12 ml.

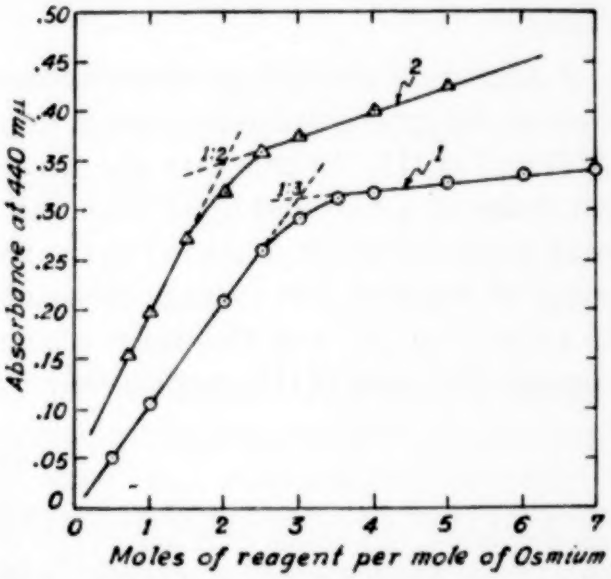

Fig. 6. Determination of the reaction ratios of reagent to (1) osmium(VIII) and (2) osmium(VI) by the molar ratio method. Concentrations of osmium(VIII) and osmium(VI) were kept constant at $2.09 \cdot 10^{-5}$ *M* and $3.46 \cdot 10^{-5}$ *M* respectively and varying amounts of reagent were added.

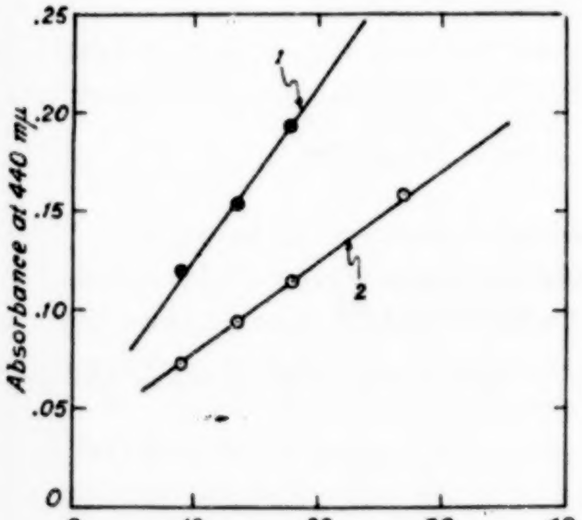

Fig. 7. Determination of the ratio of reagent to osmium(VI) by the slope ratio method. $Slope_1$ (reagent excess) = 1.44; $slope_2$ (osmium excess) = 0.73.

$$\frac{Slope_1}{Slope_2} = 1.97,\ i.e.,\ \text{a ratio of } 1:2 \text{ (approx.)}.$$

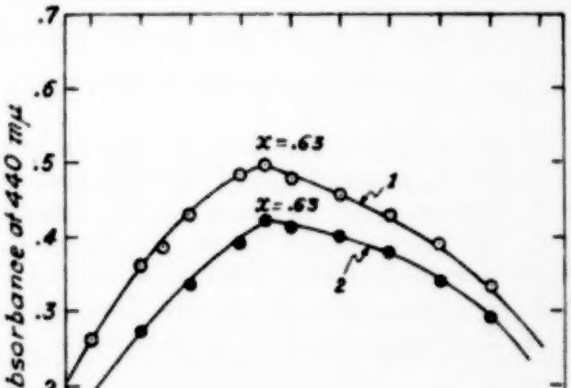

Fig. 8. Absorbance of mixtures of non-equimolecular solutions. Curve 1. $0.223 \cdot 10^{-3}$ *M* osmium(VI); $0.446 \cdot 10^{-3}$ *M* *o*-aminophenol-*p*-sulphonic acid (sodium salt). Curve 2. $0.191 \cdot 10^{-3}$ *M* osmium(VI); $0.382 \cdot 10^{-3}$ *M* *o*-aminophenol-*p*-sulphonic acid (sodium salt).

Dissociation constant of the osmium(VI)–reagent complex

The dissociation constant of the complex was evaluated from a study of the absorptions of the mixtures of non-equimolecular solutions. The colour of the solutions was developed as described above. From the data in Fig. 8, the dissociation constant, as calculated from Job's equation[1], is 1.2×10^{-7} at 34°.

Note

1-Amino-8-naphthol-3,6-disulphonic acid has been examined in exactly the same way as the monosulphonic acid for the spectrophotometric determination of osmium-(VI) and (VIII). In this case the optimum conditions are 4 ml of reagent solution, a pH range of 4.5–6 and a 2-h standing time for colour development. The absorption maximum occurs at 480 mμ; both reagents have the same optimum concentration range of osmium. The average dissociation constant with the disulphonic acid reagent is $1.2 \cdot 10^{-9}$ at 36° and the molar extinction coefficients are 14930.7 and 16642.5 for osmium(VI) and (VIII) respectively.

SUMMARY

o-Aminophenol-*p*-sulphonic acid is suggested as a very sensitive reagent for spectrophotometric determination of osmium (VI) and (VIII) at pH 2.5–4. The absorption maximum is at 440 mμ and the optimum concentration range is from 2 to 8 p.p.m. of osmium. Moderate amounts of Pd^{+2}, Ir^{+4}, WO_4^{-2}, Cr^{+3}, Zn^{+2}, Zr^{+4}, Mg^{+2}, Ba^{+2} and Sr^{+2} do not interfere.

RÉSUMÉ

L'acide *o*-aminophénol-*p*-sulfonique constitue un réactif très sensible pour le dosage spectrophotométrique de l'osmium octavalent et de l'osmium hexavalent. Absorption maximum à 440 mμ. Concentration optimum comprise entre 2 et 8 p.p.m. d'osmium.

ZUSAMMENFASSUNG

Für die spektrophotometrische Bestimmung von Osmium(VI) und Osmium(VIII) hat sich *o*-Aminophenol-*p*-sulfosäure als sehr empfindliches Reagenz erwiesen. Der günstigste Konzentrationsbereich liegt bei 2 bis 8 p.p.M. Osmium; Absorptionsmaximum bei 400 mμ.

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS

V. A SIMPLIFIED SCHEME FOR THE DETECTION OF COMMON ANIONS

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A systematic and comprehensive scheme[1] of qualitative analysis for anions has been put forward from this laboratory. In this scheme a large number of anions derived both from the common and rare-elements have been included and therefore, only a fairly advanced student can be expected to tackle the problem of detecting anions in such complex mixtures. The scheme can, however, be simplified to meet the requirements of the less advanced student of chemical analysis whose knowledge with regard to the analytical behaviour of elements is limited. The following procedures and table show how the original scheme can be modified to provide for the detection of only the common anions. The detection of anions by this method will enable the student not only to do this part of the work systematically and therefore, with greater confidence, but also to tackle more easily the detection of anions in certain combinations more easily. It will be seen from the table that the detection of acids in the following combinations can be carried out with much greater ease than by the usual methods. 1. Ferro and ferricyanides. 2. Fluoride and oxalate. 3. Sulphite, sulphate and thiosulphate. 4. Arsenite, arsenate and phosphate. Tests for borate, acetate, nitrate and nitrite, which were not included in the more comprehensive scheme, have been included in this simplified scheme.

PROCEDURES

I. 2–3 g of the mixture is boiled with 8–10 g of sodium carbonate (AnalaR quality) and nearly 100 ml of water for about 10 min and then filtered. The filtrate will contain the sodium salts of practically all acids, with the exception of certain acids, which form part of insoluble salts like sulphides of copper and zinc groups, silver halides, etc.

II. The sodium carbonate filtrate is treated with excess of lead carbonate, boiled, cooled to room temperature and filtered. A black or grey precipitate shows the presence of sulphide. The sulphides of arsenic, antimony and tin dissolve in sodium carbonate to give a mixture of thio- and oxythio-salts. Lead carbonate converts thio- and oxythio-salts into oxy-salts with the precipitation of lead sulphide.

III. A small portion of the filtrate from procedure II, is treated with a strong solution of zinc nitrate in excess, the precipitate filtered off and the neutral filtrate tested for acetate with $FeCl_3$. The rest of the filtrate from procedure II is treated with zinc acetate solution (about 1–2 *M*) until no further precipitation takes place,

TABLE I

<table>
<tr><td colspan="9">Sodium carbonate filtrate containing — S^{-2}, $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, $C_2O_4^{-2}$, F^-, $B_4O_7^{-2}$, PO_4^{-3}, SO_3^{-2}, AsO_4^{-3}, AsO_3^{-3}, SO_4^{-2}, $S_2O_3^{-2}$, Cl^-, Br^-, I^-, ClO_3^-, NO_2^-, NO_3^- and CH_3COO^-. Treat with excess of $PbCO_3$ and filter</td></tr>
<tr><td rowspan="5">Ppt: Black or grey PbS. Confirms S^{-2}</td><td colspan="8">Filt: Rest of the anions. Treat a small portion of the solution with zinc nitrate solution in excess, filter off the precipitate and test for acetate with $FeCl_3$ in the filtrate. Treat the remaining portion with $Zn(CH_3COO)_2$ solution in excess heat to boiling and filter</td></tr>
<tr><td colspan="4">Ppt: Zinc salts of $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$, $C_2O_4^{-2}$, $(F)^-$, PO_4^{-3}, AsO_4^{-3}, AsO_3^{-3}, $B_4O_7^{-2}$, SO_3^{-2}. Treat with excess of NH_4OH and filter</td><td colspan="4">Filt: F^-, SO_4^{-2}, $S_2O_3^{-2}$, Cl^-, Br^-, I^-, ClO_3^-, (AsO_3^{-3}), NO_2^-, NO_3^- and CH_3COO^-. Test small portions for nitrite and nitrate as shown below. Add $Ca(NO_3)_2$ solution in excess and filter</td></tr>
<tr><td rowspan="3">Ppt: Zn_2-$Fe(CN)_6$ dissolve in conc. HCl and add $FeCl_3$. Blue ppt. Confirms $Fe(CN)_6^{-4}$</td><td colspan="3">Filt: (F^-), PO_4^{-3}, AsO_4^{-3}, AsO_3^{-3}, $C_2O_4^{-2}$, $B_4O_7^{-2}$, SO_3^{-2}, $Fe(CN)_6^{-3}$. Add magnesia mixture in excess, 10 ml of conc. NH_4OH and filter</td><td rowspan="3">Ppt: CaF_2. Confirm by SiF_4 test</td><td colspan="3">Filt: SO_4^{-2}, $S_2O_3^{-2}$, Cl^-, Br^-, I^-, ClO_3^-, (AsO_3^{-3}) NO_2^-, NO_3^- and CH_3COO^-. Add $Ba(NO_3)_2$ solution in excess and filter</td></tr>
<tr><td rowspan="2">Ppt: Magnesium salts of (F^-), PO_4^{-3}, AsO_4^{-3} and AsO_3^{-3}. Dissolve the precipitate in dil. CH_3COOH and add excess of $Ca(NO_3)_2$ solution and filter</td><td colspan="2">Filt: $C_2O_4^{-2}$, $B_4O_7^{-2}$, SO_3^{-2} and $Fe(CN)_6^{-3}$. Add $Ca(NO_3)_2$ and $Ba(NO_3)_2$ solutions in excess and filter</td><td rowspan="2">Ppt: White $BaSO_4$ insoluble in conc. HCl shows SO_4^{-2}</td><td colspan="2">Filt: $S_2O_3^{-2}$, Cl^-, Br^-, I^-, ClO_3^-, (AsO_3^{-3}), NO_2^-, NO_3^- and CH_3COO^-. Add $AgNO_3$ solution in excess and filter</td></tr>
<tr><td>Ppt: Ca and Ba salts of $C_2O_4^{-2}$, SO_3^{-2} and BO_2^-. Treat with dil. acetic acid and filter</td><td>Filt: $Fe(CN)_6^{-3}$ and BO_3^{-3} acidify the solution with acetic acid and filter</td><td>Ppt: Silver salts of S^{-2} (from $S_2O_3^{-2}$), Cl^-, Br^-, I^- and (AsO_3^{-3}). Test a portion of the ppt. with Zn + HCl for S^{-2}, then treat with 1 N HNO_3, heat and filter</td><td>Filt: ClO_3^-, NO_3^-, NO_2^- and CH_3COO^-. Test only for ClO_3^- with $NaNO_2$ as usual</td></tr>
</table>

<table>
<tr>
<td></td>
<td>Ppt: CaF_2 Confirm by SiF_4 test</td>
<td>Filt: PO_4^{-3}, AsO_4^{-3} and AsO_3^{-3}. Neutralize the acid with NaOH and add about 30 ml of 1 *N* Na_2S reagent and filter</td>
<td colspan="2" rowspan="2">Ppt: Ca and Ba salts of $C_2O_4^{-2}$ and SO_3^{-2}. Boil with 10 ml of 10% Na_2CO_3 solution and filter off the ppt. of $CaCO_3$ and $BaCO_3$. Acidify the filtrate with CH_3COOH and add $Ca(NO_3)_2$ in excess. Filter</td>
<td rowspan="3">Filt: BO_2^-. Add $AgNO_3$ and heat. Brown ppt. of Ag_2O. Confirms $B_4O_7^{-2}$</td>
<td rowspan="3">Ppt: Zinc ferricyanide dissolve in HCl and add $FeSO_4$. Blue ppt. Confirms $Fe(CN)_6^{-3}$</td>
<td rowspan="3">Filt: BO_3^{-3}. Test with $AgNO_3$ as before</td>
<td rowspan="3"></td>
<td rowspan="3"></td>
<td rowspan="3">Ppt: Silver salts of Cl^-, Br^- and I^-. Test as usual</td>
<td rowspan="3">Filt: AsO_3^{-3} + HNO_3 and Ag^+. Add dil. HCl and filter off AgCl. In the filtrate add Na_2S and HCl. Yellow ppt. Confirms AsO_3^{-3}</td>
<td rowspan="3"></td>
</tr>
<tr>
<td rowspan="2">Ppt: Phosphate of Ca and Mg. Dissolve in HNO_3 and test for PO_4^{-3} by adding amm. molybdate. Yellow ppt. Confirms PO_4^{-3}</td>
<td colspan="2">Filt: Thiosalts of AsO_3^{-3} and AsO_4^{-3}. Treat with equal volumes of 2 *N* HCl, shake and filter</td>
</tr>
<tr>
<td>Ppt: Yellow As_2S_3 insoluble in 6 *N* HCl shows AsO_3^{-3}</td>
<td>Filt: Thiosalt of AsO_4^{-3}. Add conc. HCl and heat to boiling. Yellow ppt. of As_2S_5. Confirms AsO_4^{-3}</td>
<td>Ppt: CaC_2O_4. Confirm as usual</td>
<td>Filt: SO_3^{-2} add bromine water, HCl and $Ba(NO_3)_2$ white ppt. Confirms SO_3^{-2}</td>
</tr>
</table>

Test for NO_2: Acidify a portion with dilute H_2SO_4 and heat. Brown fumes confirms NO_2^-.
Test for NO_3: Remove the halogens by Ag_2SO_4 in a portion and test for NO_3^- by the ring test as usual.

boiled for 2–3 minutes and filtered. This will precipitate $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$, AsO_4^{-3}, SO_3^{-2}, $C_2O_4^{-2}$, PO_4^{-3} and $B_4O_7^{-2}$ completely and F^-, AsO_3^{-3} partially. The precipitate is washed 5–6 times with distilled water, only the first one or two washings being added to the main filtrate, the rest rejected to avoid increasing the volume unnecessarily.

The precipitate is divided into 3 sub-groups as follows: a. It is treated with excess of ammonium hydroxide, warmed and filtered. For satisfactory separation the final strength of the ammonium hydroxide should be between 2–6 *N*. The undissolved portion is tested for $Fe(CN)_6^{-4}$. b. The ammoniacal filtrate from sub-group (a) is treated with magnesia mixture in slight excess and about 10 ml of concentrated ammonia is added to precipitate arsenite completely. It is heated nearly to boiling and filtered after 5–10 minutes. The precipitate will contain magnesium salts of F^-, AsO_3^{-3}, AsO_4^{-3} and PO_4^{-3}. The precipitate is washed with 2 *N* ammonium hydroxide and is tested for these acids as shown in the table. c. The filtrate from sub-group (b) is treated with excess of barium and calcium nitrate solutions, heated nearly to boiling and filtered. The precipitate contains the calcium and barium salts of $C_2O_4^{-2}$, BO_2^- and SO_3^{-2} and the filtrate soluble salts of $Fe(CN)_6^{-3}$ and borate. The precipitate and filtrate are analysed as shown in the table.

IV. Two small portions of the neutral filtrate from procedure III are tested for nitrite and nitrate as shown in the table. The rest of the filtrate is treated with calcium nitrate solution, any precipitate of calcium fluoride is filtered off and tested for fluoride as usual.

The filtrate from calcium fluoride is treated with barium nitrate solution, heated to boiling and filtered. The presence of sulphate in the precipitate is confirmed by treating it with concentrated hydrochloric acid. Barium thiosulphate is not precipitated owing to its tendency to form supersaturated solution.

V. The neutral filtrate from procedure IV is treated with excess of silver nitrate solution and filtered. The precipitate will contain the silver salts of S^{-2} (from $S_2O_3^{-2}$), Cl^-, Br^-, I^- and (AsO_3^{-3}) and the filtrate ClO_3^-. The precipitate and the filtrate are analyzed as shown in the table.

SUMMARY

The original comprehensive scheme for the detection of anions has been simplified for the systematic detection of common anions.

RÉSUMÉ

Un schéma d'analyse qualitative simplifié est proposé pour l'identification des anions courants.

ZUSAMMENFASSUNG

Es wird ein vereinfachtes Schema zum Nachweis der häufiger vorkommenden Anionen beschrieben.

REFERENCES

[1] I. K. TAIMNI AND MANOHAR LAL, *Anal. Chim. Acta*, 17 (1957) 367, 372.

FLAME SPECTRA OF Sc, Y AND RARE-EARTH ELEMENTS*

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INTRODUCTION

The detection and determination of small quantities of rare-earth elements is of growing importance in nuclear fuel technology. Several of these elements, which accumulate in nuclear reactors as fission products, exert an inordinately detrimental effect on the neutron economy of reactors because of their extremely large capture cross section for thermal neutrons. For this reason, especially, they are undesirable as impurities in nuclear fuels or breeder materials. Since the rare-earth elements comprise a considerable portion of the fission products in spent fuels, methods for reprocessing fuels or blanket materials must be capable of reducing the concentration of rare-earth elements to tolerable limits. Reliable methods for the estimation of elements of this group are, therefore, essential in the evaluation and control of reprocessing procedures, as well as in the operation of reactors.

Unfortunately, specific and relatively sensitive methods for the determination of the rare-earth elements are lacking. Because of the similarity of chemical properties of the elements of the rare-earth group, spectrophotometric methods, utilizing chromogenic reagents, are suitable only for estimation of the total elements of this group[1]. The characteristic absorbance spectra of the rare-earth elements are not intense enough to provide the requisite sensitivity. In fact, several of these elements (yttrium, lanthanum, and ytterbium) do not absorb light in the visible region[2]. Spectrographic methods, which are used most frequently for the analysis of mixtures of rare-earth elements, suffer from the difficulty of resolving the complex spectra[3-5]. As a result of the intensified interest in the rare-earth elements, advances have recently been made in methods of analysis pertaining to this group of elements. FELDMAN AND ELLENBURG[6] have reported a method for separation of the rare-earth elements from thorium and subsequently determining them by spectrographic means. PINTA[3] studied the flame spectra of sixteen rare-earth and closely related elements. He aspirated aqueous solutions of the elements into an air–acetylene flame and used a prism spectrograph to record the emission bands and lines on photographic plates. On the basis of this study, he developed a procedure for the determination of a number of these elements.

The objective of the present investigation was to study the complex spectra of the

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rare-earth elements and the closely related elements, yttrium and scandium, more thoroughly for the purpose, primarily, of evaluating, extending and improving flame photometric methods for the estimation of the elements of this group. Chelates of the different rare-earth elements with 2-thenoyltrifluoroacetone (TTA) were extracted into an organic solvent[7], the organic extract was introduced into an oxy–hydrogen flame and the individual flame spectra were recorded by a flame photometer. Furthermore, the flame spectra of elements of this group in aqueous media were photographically recorded with a prism spectrograph to provide data for fixing the position accurately of the characteristic bands and lines. By use of an organic medium, the emissivity was greatly enhanced; in many cases, the enhancement was of the order of 100 times the emissivity attainable with aqueous solutions. By these means, as has been reported in the case of lanthanum[8], more intense, detailed spectra were obtained whereby the limits of detection of the elements can be extended. Lower concentrations of the several elements can thereby be estimated than was previously possible.

EXPERIMENTAL WORK

Apparatus

Oak Ridge National Laboratory recording flame spectrophotometer, Model No. Q-1457A[9]. This is a single-beam, high-sensitivity instrument equipped with RCA 6217 and Farnsworth 16PMI multiplier phototubes and a modified atomizer-burner from a Beckman flame photometer. Lacquer was removed from the adjusting screws used to align the palladium capillary of the burner and the screws were then silver-soldered in place. This modification was made to insure that the burner would function properly when organic solvents were aspirated into it. In addition, the flame was shielded to mask out light from the luminous cone and thus minimize interference from CH and C_2 bands when organic media are used to introduce elements into the oxy-hydrogen flame.

Reagents

4-Methyl-2-pentanone (hexone), practical grade. 2-Thenoyltrifluoroacetone (TTA), 0.1 *M* in hexone. This reagent was prepared by dissolving 22 g of technical-grade TTA in hexone, and then diluting the solution to one liter with hexone. It is stored in a cool place away from light.

Stock solutions of the rare-earth elements, 1 mg per ml. An amount of the rare-earth oxide required to give 50 mg of the element was dissolved in 10 ml of conc. HCl. This solution was transferred to a 50-ml volumetric flask and diluted to volume with 1 *N* HCl. (The oxides of rare-earth elements were obtained from Lindsay Chemical Division, American Potash and Chemical Corporation).

Acetate buffer solution, 5 *M*, pH 5.5. This reagent was prepared by dissolving 385 g of ammonium acetate in water and diluting to 600 ml with water. The pH of the solution was then adjusted to 5.5 by addition of 5 *N* acetic acid, after which it was diluted to one liter with water.

Recording of spectra

Solutions of the chelates of the rare-earth elements with 2-thenoyl-trifluoroacetone (TTA) in 4-methyl-2-pentanone (hexone) were used in recording the flame spectra of the several elements. These solutions were prepared as follows: an aliquot of the stock solution of the element which usually contained one mg of the element (exceptions: Pr, 10 mg; Nd, 2 mg) was transferred to a 60-ml separatory funnel. Eight ml of 5 *M* acetate buffer solution (pH 5.5) was added and the solution was diluted to 20 ml with water. A 20-ml portion of the 0.1 *M* solution of TTA in hexone was then added and the separatory funnel was shaken for three minutes. After the phases had separated, the organic phase was transferred to a flask and used for the determination of the flame spectrum.

The flame spectra were recorded by means of an ORNL single-beam recording flame spectrophotometer. The organic solution of the element was aspirated into the flame and the emissivity was continuously recorded over the wave length range from 380 to 900 mμ.

Operating conditions were as follows:

Sensitivity control, High; Phototube resistor, 5 MegOhms; Phototube, Blue sensitive, RCA-6217, 80 V/dynode; Red sensitive, 16-PMI, 80 V/dynode; Slit width, 0.25 mm; Spectral slit width, 1.6 mμ; Gas flow rate, Oxygen, 5100 cm^3/min; Hydrogen, 3600 cm^3/min.

Over the wave length range from 380 to 700 mμ, the blue-sensitive phototube, RCA-6217, was used, while, at wave lengths from 700 to 900 mμ emissivity measurements were made with the red-sensitive multiplier phototube, Farnsworth 16-PMI[10]. As indicated above, all spectra were recorded with a phototube potential of 80 V per dynode, even though the phototubes will operate satisfactorily at 100 V per dynode and, at the higher voltage, the sensitivity (emissivity per unit of element per ml in test solution) is 10 times as great as at 80 V per dynode. The lower voltage was used in recording the spectra because, under the operating conditions given, at the higher voltage prominent bands or lines would be off scale. In calculating the maximum spectral intensities, which are listed in Table I, the emissivities at 100 V per dynode were used. These were computed from the data taken at 80 V per dynode with a slit width of 0.25 mm, utilizing the known constant ratio between emissivity at 100 V per dynode and emissivity at 80 V per dynode. This ratio is independent of wave length.

TABLE I

WAVE LENGTHS AND RELATIVE SPECTRAL INTENSITY OF THE RARE-EARTH ELEMENTS BY FLAME EMISSION

Conditions: ORNL Flame Spectrophotometer, Multiplier phototube, blue, RCA — 6217, red, Farnsworth — 16-PMI; Voltage per dynode — 100; Slit width, 0.25 mm; Gas flow rate: O_2, 5100 cm^3/min, H_2, 3600 cm^3/min; Medium, TTA in hexone, 0.1 *M*;
Hilger, large Littrow Spectrograph, Photograph plates: Kodak (3) 103a-F; Kodak I—N; Exposure time, 4–10 minutes; Medium, HCl, 1 *N*.

Element	*Spectrographic line and band maxima, mμ*	*Spectrophotometric*		
		Line and band maxima, mμ	*Width of band, mμ*	*Relative spectral intensity scale div./μg/ml*
Scandium	450.3	450	448–485	1
	453.6	453	448–485	2
	457.1	457	448–485	2
	460.7	462	448–485	2
	467.3	466	448–485	7
	470.7	n	—	—
	n	473	448–485	7
	474.2	475	448–485	5
	485.8	486	485–500	20
	489.3 NL	n	—	—
	509.7	n	—	—
	513.4	n	—	—
	517.1 NL	n	—	—
	573.7	574	570–635	5
	577.4	578	570–635	14
	581.2	582	570–635	17
	584.9	586	570–635	16
	592.3	592	570–635	10
	596.5	595	570–635	6
	603.2	602	570–635	88
	607.2	607	570–635	170
	610.9	610	570–635	130
	614.8	n	—	—
	619.3	n	—	—
	644.3	642	640–675	1
	648.2	647	640–675	2
	649.6	650	640–675	2
	656.7	657	640–675	2
Yttrium	470.7	468	464–480	4
	481.8	484	480–500	12
	505.1	506	502–560	3
	507.9	509	502–560	3
	527.5	527	502–560	1
	573.0	n	—	—
	575.6	575	565–630	4

TABLE I (Continued)

Element	*Spectrographic line and band maxima, mμ*	*Spectrophotometric*		
		Line and band maxima, mμ	*Width of band, mμ*	*Relative spectral intensity scale div./μg/ml*
Yttrium	593.9	n	—	—
	595.6	n	—	—
	597.8	598	565–630	80
	600.4	n	—	—
	603.7	n	—	—
	613.7	614	565–630	80
	616.5	n	—	—
	618.2	n	—	—
	620.0	n	—	—
Lanthanum	437.4	437	435–450	8
	441.8	442	435–450	9
	443.6	n	—	—
	538.0	n	—	—
	540.7	n	—	—
	543.2	n	—	—
	545.8	545	537–556	3
	560.2	560	557–585	11
	562.8	562	557–585	11
	586.8	n	—	—
	701.1	n	—	—
	702.4	n	—	—
	704.1	n	—	—
	705.5	n	—	—
	707.0	n	—	—
	708.5	n	—	—
	710.1	n	—	—
	713.2	n	—	—
	716.3 NL	n	—	—
	719.4	n	—	—
	738.0	n	—	—
	740.6	741	735–765	8
	743.7	744	735–765	8
	762.5	n	—	—
	787.7	n	—	—
	791.1	791	785–820	8
	794.5	795	785–820	7
	808.6	n	—	—
	812.2	n	—	—
	815.9	n	—	—
	845.4	n	—	—
	849.0	n	—	—
	852.7	n	—	—
	856.4	n	—	—
Praseodymium	n	416	410–750	0.1
	n	438	410–750	0.3
	n	452	410–750	0.3
	n	460	410–750	0.3
	n	467	410–750	0.3
	n	473	410–750	0.2
	n	482	410–750	0.3
	n	492	410–750	0.3
	n	502	410–750	0.2
	n	512	410–750	0.3
	n	518	410–750	0.4
	n	530	410–750	0.3

TABLE I (Continued)

Element	*Spectrographic line and band maxima, mμ*	*Spectrophotometric*		
		Line and band maxima, mμ	*Width of band, mμ*	*Relative spectral intensity scale div.μg/ml*
Praseodymium	535.1	n	—	—
	n	540	410–750	0.5
	n	562	410–750	0.6
	569.2	569	410–750	0.8
	576.4	577	410–750	0.8
	n	594	410–750	0.3
	602.0	n	—	—
	603.8	604	410–750	3
	n	614	410–750	0.6
	n	618	410–750	0.5
	628.0	623	410–750	0.4
	629.8	630	410–750	0.7
	636.0	637	410–750	0.6
	644.0	n	—	—
	647.6	649	410–750	0.5
	n	655	410–750	0.4
	n	664	410–750	0.3
	n	672	410–750	0.2
	681.8	n	—	—
	688.7	n	—	—
	n	695	410–750	0.4
	709.7	709	410–750	0.4
	732.2	735	410–750	0.3
	n	748	410–750	0.2
	n	830	820–840	<0.1
	849.0	n	—	—
	n	930	920–940	<0.1
Neodymium	462.5	465	460–470	0.5
	495.9	n	—	—
	513.8	515	500–585	0.5
	532.4	533	500–585	0.5
	568.0	n	—	—
	572.6	574	500–585	0.5
	597.5	n	—	—
	599.7	600	595–610	1
	621.9	622	610–730	1
	635.2	n	—	—
	637.0	n	—	—
	638.6	638	610–730	2
	644.5	645	610–730	2
	662.5	662	610–730	4
	n	700	610–730	3
	n	712	610–730	3
	741.5 NL	n	—	—
Samarium	441.9*	n	—	—
	444.2*	n	—	—
	458.2*	n	—	—
	461.5*	462	450–500	1
	467.1*	n	—	—
	472.9*	473	450–500	1
	476.0*	n	—	—
	484.2*	n	—	—
	488.4*	n	—	—
	520.1*	n	—	—

TABLE I (Continued)

Element	*Spectrographic line and band maxima, mμ*	*Spectrophotometric*		
		Line and band maxima, mμ	*Width of band, mμ*	*Relative spectral intensity scale div./μg/ml*
Samarium	527.1*	n	—	—
	603.4	n	—	—
	607.2	n	—	—
	613.7	613	570–700	8
	624.1	623	570–700	9
	639.6	638	570–700	8
	652.3	652	570–700	8
Europium	413.0*	412	410–422	1
	420.5*	420	410–422	1
	443.6*	n	—	—
	459.4*	459*	—	22
	462.7*	463*	—	18
	466.2*	466*	—	15
	564.8*	n	—	—
	576.5*	575	570–700	2
	601.8	598	570–700	13
	C	625	570–700	11
	C	648	570–700	9
	C	655	570–700	8
	C	684	570–700	3
Gadolinium	446.3	n	—	—
	448.1	n	—	—
	449.9	450	445–500	2
	461.6	n	—	—
	464.3	464	445–500	8
	479.9	n	—	—
	481.7	n	—	—
	484.4	484	445–500	2
	489.2	n	—	—
	492.8	492	445–500	4
	513.4	514	510–640	1
	540.5 NL	n	—	—
	545.0 NL	546	510–640	3
	566.5 NL	n	—	—
	568.1	n	—	—
	569.9	570	510–640	7
	580.7	n	—	—
	582.1	582	510–640	15
	591.8	n	—	—
	593.3	n	—	—
	598.7	599	510–640	27
	600.7	n	—	—
	609.1	n	—	—
	612.4	612	510–640	27
	614.3	n	—	—
	616.7	n	—	—
	619.4 NL	n	—	—
	622.4	622	510–640	32
	624.2	n	—	—
Terbium	447.2	448	445–490	1
	457.3	457	445–490	1
	460.7	460	445–490	2
	472.7*	n	—	—

TABLE I (Continued)

Element	*Spectrographic line and band maxima, mμ*	*Spectrophotometric*		
		Line and band maxima, mμ	*Width of band, mμ*	*Relative spectral intensity scale div./μg/ml*
Terbium	478.5	478	445–490	1
	514.1	515	505–640	1
	527.0	525	505–640	2
	534.7*	535	505–640	10
	560.3	560	505–640	6
	564.0*	565	505–640	7
	572.7	574	505–640	11
	585.8	n	—	—
	592.1	n	—	—
	594.1	n	—	—
	598.0	598	505–640	13
	605.7	605	505–640	8
	607.3	n	—	—
	607.9	n	—	—
	616.1	615	505–640	3
	635.1	n	—	—
Dysprosium	418.7*	n	—	—
	421.2*	n	—	—
	453.4	454	445–465	1
	456.9	457	445–465	1
	514.0	515	500–640	5
	524.7	n	—	—
	526.3*	n	—	—
	528.0	527	500–640	15
	540.0	541	500–640	11
	549.3	550	500–640	10
	569.5	n	—	—
	572.9	575	500–640	18
	583.3	584	500–640	15
	600.7	n	—	—
	605.1	608	500–640	3
Holmium	446.5 NL	n	—	—
	449.0 NL	n	—	—
	510.5	510	500–545	7
	514.3	n	—	—
	515.7*	515	500–545	10
	527.6	527	500–545	7
	532.0	532	500–545	6
	556.4	555	550–600	5
	560.9	560	550–600	9
	565.9	566	550–600	25
	569.6*	n	—	—
	572.8	n	—	—
	585.1	585	550–600	2
Erbium	498.6	n	—	—
	504.0	503	485–585	12
	506.6	n	—	—
	514.7	514	485–585	5
	545.1	546	485–585	8
	552.0	552	485–585	13
	560.8	560	485–585	8
	566.3	566	485–585	6

TABLE I (Continued)

Element	*Spectrographic line and band maxima, mμ*	*Spectrophotometric*		
		Line and band maxima, mμ	*Width of band, mμ*	*Relative spectral intensity scale div./μg/ml*
Thulium	409.4*	409	407–425	1
	410.6*	n	—	—
	418.8*	418	407–425	1
	420.4*	n	—	—
	436.0*	n	—	—
	438.6*	n	—	—
	473.4*	n	—	—
	481.5 NL	483	470–580	7
	489.3 NL	n	—	—
	493.9 NL	492	470–580	10
	522.6 NL	523	470–580	4
	532.9 NL	n	—	—
	534.8 NL	n	—	—
	539.5 NL	538	470–580	9
	541.5 NL	542	470–580	8
	553.0 NL	553	470–580	7
	558.8 NL	n	—	—
	567.6*	n	—	—
Ytterbium	398.8*	399*	—	60
	451.5 NL	n	—	—
	474.2	474	465–562	5
	475.6	n	—	—
	476.5	n	—	—
	477.4	478	465–562	7
	484.1	484	465–562	6
	496.6	497	465–562	9
	518.0	516	465–562	6
	529.6	530	465–562	12
	544.0	545	465–562	5
	555.6*	556	465–562	11
	573.3 NL	573	565–580	9
Lutetium	409.5	411	407–420	2
	468.4	468	465–480	25
	517.0	518	505–530	25
	540.5 NL	n	—	—
	599.3 (597.1–601.4) NL	600	595–605	2
	674.9 (668.8–681.0) NL	675	665–685	1

* — Line; C — bands masked by continuum; n — not observed; NL — not reported in literature.

Spectra of the same elements were also recorded photographically by means of a Hilger, large Littrow spectrograph, to take advantage of the greater resolving power of this instrument in accurately locating the position of the characteristic lines and bands. Light from the flame of the Beckman burner was focused on the entrance slit of the spectrograph by means of a lens. Strong solutions of the rare-earth elements containing 10 to 25 mg of the element per ml dissolved in 1 *N* HCl were aspirated into the flame. Kodak 1030-F(3) and 1-N plates were used to photograph the spectra. The period of exposure ranged from 4 to 10 min, depending upon the concentration and sensitivity of the element. The spectral data obtained were used in fixing the wave lengths assigned to the band maxima and lines in Tables I and II. These data were compared with literature values[11–16]. Several lines and bands which were not previously reported are indicated in Table I.

TABLE II

PRINCIPAL EMISSION BANDS AND LINES OF Sc, Y, AND RARE-EARTH ELEMENTS: RELATIVE SPECTRAL INTENSITY AND INTERFERENCES

Element	*Wave length, mμ*	*½ Band width, mμ*	*Sensitivity, scale div./μg/ml*	*Interference scale div./μg/ml*
Scandium	607	10	170	(a)
Yttrium	482	5	12	Tm-7; Yb-6; Gd-2
	598	8	80	Gd-27; Eu-13; Tb-13; Sm-6; Dy-2; Lu-2; Pr-1
	614	8	80	Gd-27; Sm-8; Eu-6; Tb-3; Pr-1
Lanthanum	442	5	9	None
	741	10	8	None
	791	10	8	None
Praseodymium	604	5	3	Y-40; Gd-20; Tb-8; Sm-6; Dy-3; Nd-1
Neodymium	663	8	4	Eu-4; Sm-4
	700	15	3	None
	712	8	3	None
Samarium	614	18	8	Y-80; Gd-27; Eu-5; Tb-3; Dy-2
	624	10	9	Y-40; Gd-32; Eu-11; Tb-2
	640	10	8	Eu-8; Gd-2; Nd-1
	652	10	8	Eu-8; Nd-1
Europium	459	Line	22	Tb-2; Sm-1
	463	Line	18	Gd-8; Tb-2; Sm-1
	466	Line	15	Gd-8; Tb-2
Gadolinium	464	5	8	Eu-18; Sm-1
	622	20	32	Y-40; Eu-11; Sm-9; Dy-2; Tb-2; Nd-1
Terbium	535	5	10	Yb-10; Tm-5; Ho-3; La-3; Y-1
	573	5	11	Dy-18; Yb-9; Gd-7; Er-2; Tm-2; Y-2
	598	5	13	Y-80; Gd-27; Eu-13; Sm-4; Pr-1
Dysprosium	528	5	15	Yb-10; Ho-6; Tm-2
	540	5	11	Tm-9; Tb-8; Gd-2; Yb-2
	549	5	10	Er-8; Tm-8; La-3; Gd-2; Tb-2
	573	10	18	Ho-10; Yb-9; Tb-8; Gd-5
	583	5	15	Gd-15; Tb-8; Ho-4; Y-4
Holmium	516	8	10	Lu-20; Er-5; Dy-5; Tm-2; Y-2; Yb-2
	532	5	6	Yb-12; Tm-7; Dy-5; Tb-4; Gd-1
	566	10	25	La-8; Gd-7; Tb-7; Er-6; Tm-5; Yb-4

(a) Easily separated; therefore, mutual interferences are not listed.

TABLE II (Continued)

Element	*Wave length, mμ*	*½ Band width, mμ*	*Sensitivity scale div./μg/ml*	*Interference scale div./μg/ml*
Erbium	504	12	12	Y-3; Yb-2
	552	18	13	Dy-8; Tb-5; Yb-5; Gd-3; La-3
Thulium	482	5	7	Y-12; Yb-6; Gd-1
	494	10	10	Gd-4; Yb-2
	540	12	9	Dy-11; Gd-3; La-3; Ho-2; Tb-2; Yb-2
Ytterbium	399	Line	60	None
Lutetium	468	5	25	Eu-10; Gd-4; Y-4; Tb-1
	517	5	25	Ho-10; Er-6; Dy-5; Y-2

DISCUSSION

Flame spectra of scandium, yttrium and all rare-earth elements except cerium and promethium are presented in Fig. 1. These spectra were recorded with an Oak Ridge National Laboratory grating spectrophotometer[9]. Hexone solutions containing 50 μg per ml of the elements were, with two exceptions, used in obtaining all spectra; for neodymium and praseodymium, solutions containing 100 and 500 μg per ml of the element, respectively, were utilized. For several of the elements, the spectra of which contain exceptionally strong bands or lines, spectra were also recorded with less concentrated solutions in order to retain the intense lines or bands on scale. Broken lines are used in plotting these spectra. The same wave length scale is used in plotting all spectra, in order to facilitate comparison between spectra.

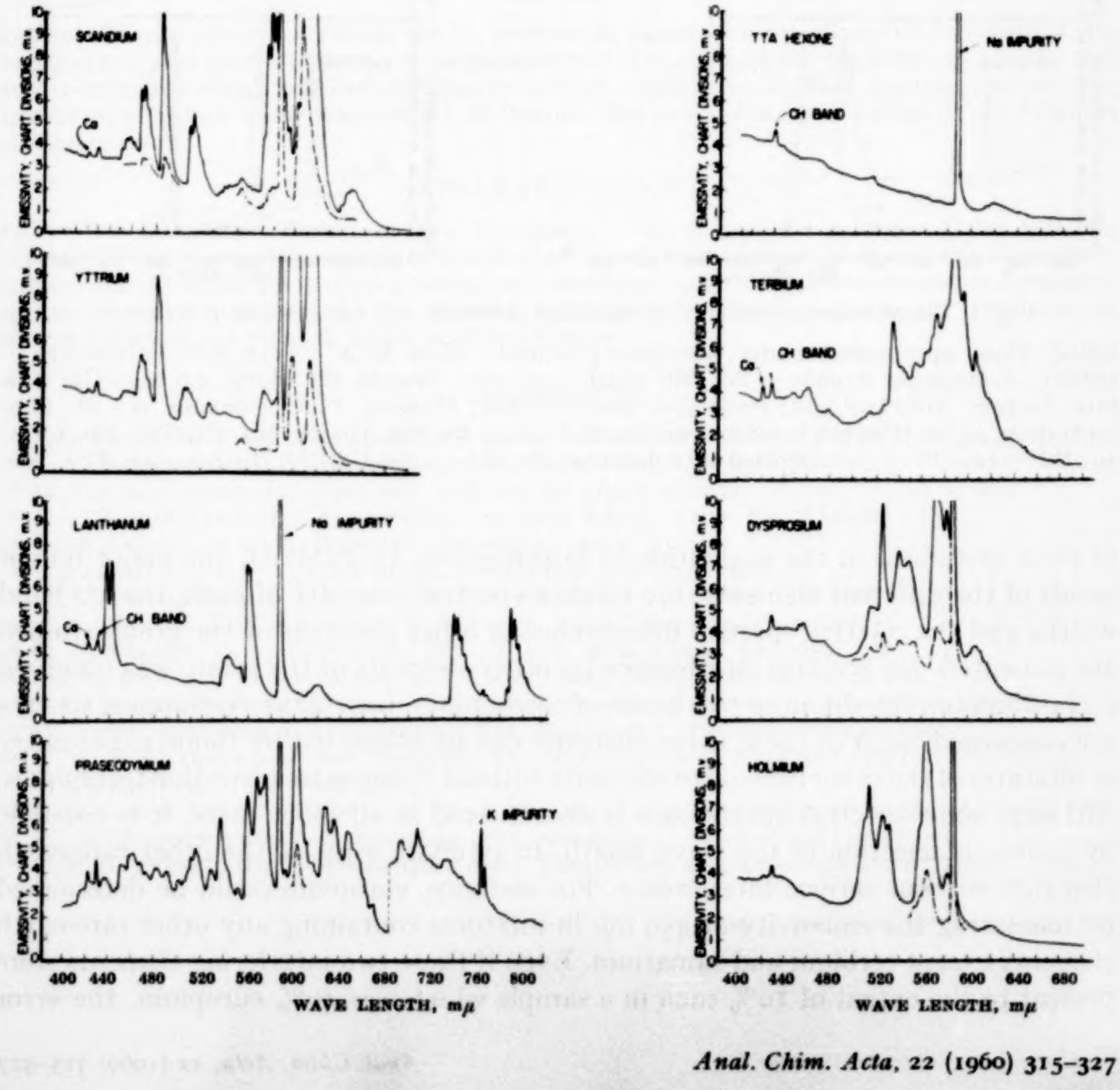
The background spectrum is also shown in Fig. 1. In recording this spectrum, a solution of TTA in hexone was aspirated into the flame. Hexone rather than aqueous solutions were used in making spectral measurements with the flame spectrophotometer because of the pronounced enhancement of emissivity attainable with this medium. When hexone is used, however, the flame spectrum contains a CH band at 431 mμ and C_2 bands at 473, 517, 564, and 619 mμ which will obscure portions of the desired elemental spectra unless they are eliminated. It was found that this could be accomplished either by lowering the flame or by shielding the flame to exclude light from the luminous inner cone. The latter method proved to be the most practical and essentially elimitated the CH and C_2 bands from the back-ground spectrum without decreasing the sensitivity of spectral measurements appreciably. Although the band structure is practically eliminated, a certain amount of continuous background radiation is observed. The intensity of this background radiation is a maximum in the near ultraviolet region and is degraded toward the red region of the spectrum. A sodium line is also observed due to sodium as an impurity in the hexone. Many of the spectra of the rare-earth elements also exhibit a calcium line at 423 mμ, due, evidently, to traces of calcium in some of their oxides.

The wave length maximum of each line or band of the spectra together with the band widths and the relative spectral intensity of each line or band are tabulated in

Table I. The positions of lines or of band crests were accurately fixed from spectral data recorded photographically with a prism spectrograph, whereas spectra obtained by the use of the flame spectrophotometer were used to establish the band widths. The relative spectral intensity was determined by measuring the peak height in scale divisions, and then dividing this value by the concentration of the element in μg per ml. The peak height was measured by averaging the background height on either side of the band and then using this average height as the base line from which to measure the height of the bandcrest.

Although organic solutions were found to be advantageous in making flame spectrophotometric measurements, aqueous solutions are to be preferred in spectral measurements with a prism spectrograph because of the period of time required, from 4 to 10 min, to record the spectra photographically. When an organic solution is burned for extended periods of time, difficulties are encountered due to clogging of the burner which are avoided if an aqueous solution is used. The spectrographic measurements were, therefore, made with aqueous solutions.

By comparison of the spectral data appearing in Table I, deductions can be made relative to the interference of various elements of this group with the estimation of a particular element at a specific wave length. The band widths are included because



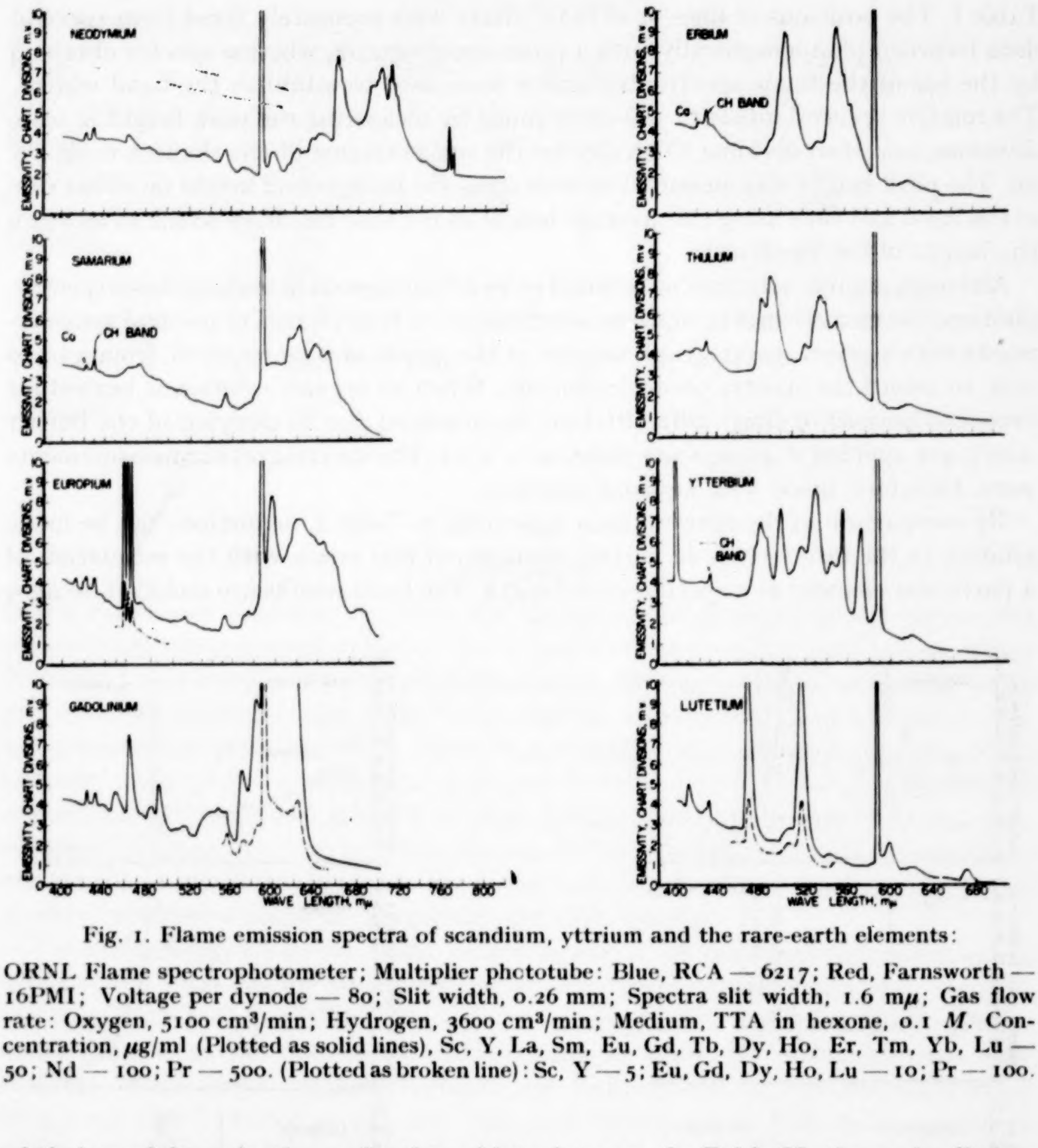


Fig. 1. Flame emission spectra of scandium, yttrium and the rare-earth elements:

ORNL Flame spectrophotometer; Multiplier phototube: Blue, RCA — 6217; Red, Farnsworth — 16PMI; Voltage per dynode — 80; Slit width, 0.26 mm; Spectra slit width, 1.6 mμ; Gas flow rate: Oxygen, 5100 cm^3/min; Hydrogen, 3600 cm^3/min; Medium, TTA in hexone, 0.1 *M*. Concentration, μg/ml (Plotted as solid lines), Sc, Y, La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu — 50; Nd — 100; Pr — 500. (Plotted as broken line): Sc, Y — 5; Eu, Gd, Dy, Ho, Lu — 10; Pr — 100.

of their usefulness in the evaluation of interferences. In Table II, the major line or bands of the different elements, the relative spectral intensity of each, the 1/2-band widths and the relative spectral interference of other elements of the group studied are presented. No spectral interference by other elements of the group was observed for lanthanum, ytterbium, or two bands of neodymium. In so far as overlapping spectra are concerned, each of these three elements can be estimated by flame photometry in mixtures of the other rare-earth elements without recourse to separation techniques. Although some spectral interference is encountered in all other cases, it is possible, by judicious selection of the wave length, to estimate some of the other rare-earth elements without serious interference. For instance, europium could be determined by measuring the emissivity at 459 mμ in mixtures containing any other rare-earth elements except terbium and samarium. Even if these two interfering elements were present to the extent of 10% each in a sample which was 40% europium, the error

due to spectral interference would be of the order of 3% of the true value for europium. Only europium and neodymium will interfere with the estimation of samarium at 652 mμ. If the ratio of the interfering elements and samarium does not exceed 1 to 20, the error will not exceed 5% of the true value. A study of methods for the estimation of individual elements in this group is in progress.

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SUMMARY

Flame spectra are presented of scandium, yttrium and the rare-earth elements, except cerium and promethium. These elements were extracted with a solution of 2-thenoyltrifluoroacetone (TTA) in 4-methyl-2-pentanone (hexone) and their spectra in the organic medium were subsequently recorded by means of a flame spectrophotometer. The precise wave length and relative spectral intensity of each line and band are tabulated. Included, also, are the 1/2-band widths and the relative spectral interferences of other elements of the group with the emission of measurement of the bands and lines listed. Operating conditions, applicability and limitations of the method in the estimation of some of the rare-earth elements are given.

RÉSUMÉ

Les auteurs ont effectué une étude sur les spectres de flamme du scandium, de l'yttrium et des terres rares, sauf ceux du cérium et du prométhéum. Les chélates de ces éléments avec la thénoyl-2-trifluoroacétone sont extraits dans la méthyl-4-pentanone-2; leurs spectres sont enregistrés au moyen d'un spectrophotomètre de flamme. Des recherches sur le dosage de ces éléments sont en cours.

ZUSAMMENFASSUNG

Es werden die Flammenspektren von Scandium, Yttrium und der seltenen Erden mit der Ausnahme von Cer und Promethium beschrieben. Die Chelate dieser Elemente mit Thenoyl-2-trifluoraceton werden mit Methyl-4-pentanon-2 extrahiert und die Spektren mit einem Flammenspektrophotometer registriert. Die Anwendungsmöglichkeit dieser Methode zur Bestimmung einiger Elemente der seltenen Erden wird beschrieben.

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REACTIONS BETWEEN ALKALOIDS AND TETRAPHENYLBORON AND THEIR ANALYTICAL APPLICATION

A HETEROMETRIC STUDY

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INTRODUCTION

A heterometric study of the reaction of alkaloids and other large nitrogen-containing compounds in potassium iodide solution with bismuth nitrate has already been carried out[1]. The reaction could be studied only at very low pH values. Similar reactions could be investigated at higher pH values if tetraphenylboron (TPB) was used as titrant instead of bismuth. We present here a study of reactions of large nitrogen-containing compounds (A) with TPB at pH values 1–9. The results are interesting because they throw light on the behaviour of these compounds at higher pH values. The use of TPB has an additional advantage: only very low concentrations of bismuth could be used as titrant, because at higher concentrations bismuth iodide was precipitated. No such limitations existed in the case of TPB; also, high concentrations of TPB permitted the inclusion of the less sensitive compounds.

During the last seven years, different methods have been suggested for the analysis of basic heterocyclic nitrogen compounds of smaller molecules with TPB[2], *e.g.* choline and its derivatives have been determined as well as many alkaloids. The TPB-N-salt compounds appeared to be insoluble in ether, $CHCl_3$ and CCl_4, but were soluble in acetone. Generally the salt extract was evaporated and the salt identified by its melting point. In another method the salt was dissolved in perchloric acid and then the TPB was titrated with silver nitrate potentiometrically; often 100 mg or more of the insoluble compound was needed for the analysis.

We found that the sensitivity of TPB towards the nitrogen-containing compounds was about three times less than that of bismuth. The individual character and structure of the different compounds was also more pronounced with bismuth. Nevertheless, some aspects could be better studied with TPB. We were able to establish that the order of sensitivity of the different compounds towards TPB was sometimes entirely different than in the case of bismuth iodide. Thus acriflavine and rivanol, which were the least sensitive with bismuth iodide, were the most sensitive with TPB. This is of course caused by the different character of the anions used. A comparison of TPB with bismuth iodide therefore gives information on the structural requirements in both cases.

EXPERIMENTAL

Instrumentation

The same instrumentation and the same working conditions were observed as in previous heterometric investigations[3].

Reagents

Altogether 13 nitrogen-containing compounds were studied. The same reagents were used as in the similar work with bismuth iodide.

Sodium tetraphenyl boron, Hopkin & Williams, Ltd. A 0.01 *M* aqueous standard solution was prepared, from which more dilute solutions were obtained.

8-Hydroxyquinoline, "Baker Analyzed".

RESULTS AND DISCUSSION

The results of the experiments carried out are presented in Tables I and II. The course of the reactions in some of these experiments are presented in Fig. 1 (Table I) and in Fig. 2 (Table II). The tables show the final compounds (↓↓) as well as the intermediate compounds (↓).

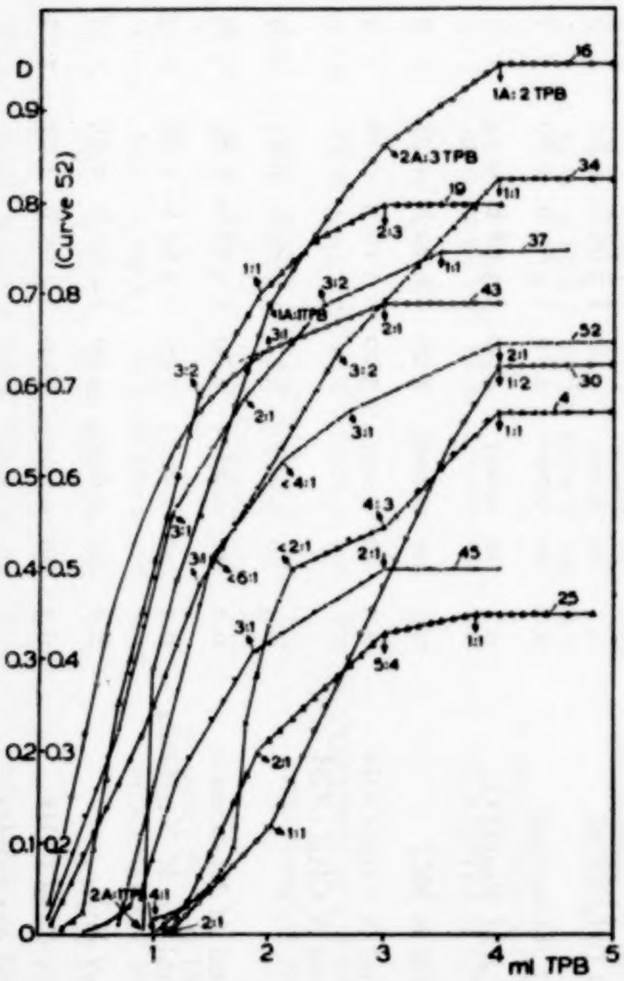

Fig. 1. Titrations of nitrogen compounds with sodium-tetraphenylboron (Table I).

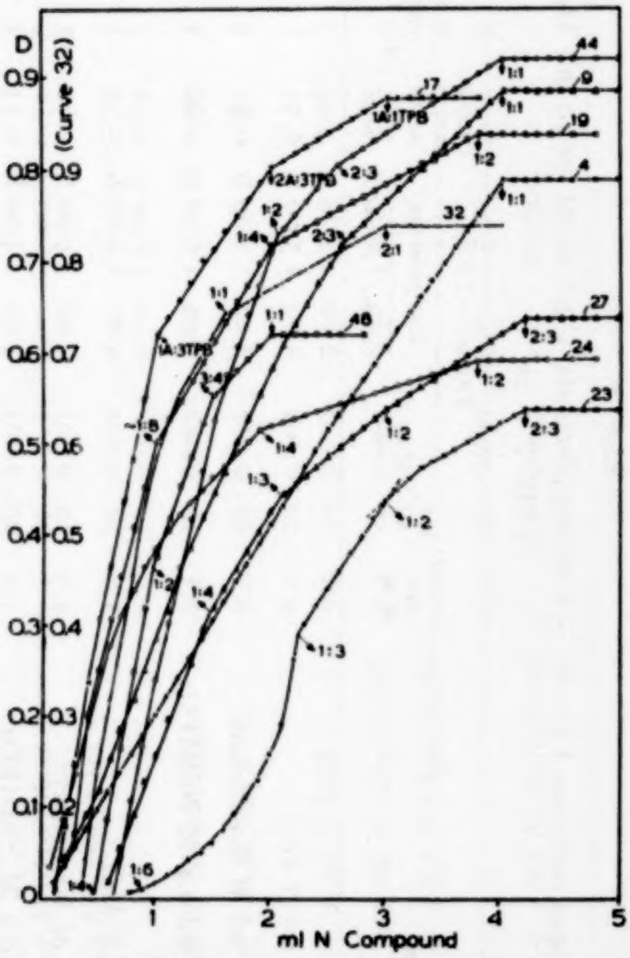

Fig. 2. Titrations of sodium-tetraphenylboron with nitrogen compounds (Table II).

Sensitivity

In the tables the nitrogen-containing compounds are shown according to decrease in molar sensitivity. The order of sensitivity in mg does not always agree with the order of molar sensitivity. Acriflavine, which appears first in Table I, was among the least sensitive with bismuth iodide. Approximately one mg was necessary for the determination of the most sensitive compounds, while in the case of the least sensitive oxine, about 5 mg were needed. On the other hand, nitron, cinchonine and quinine were among the most sensitive compounds, both with TPB and bismuth iodide. Antipyrine and atropine belong to the less sensitive alkaloids with both reagents.

TABLE I

General composition: *a* ml K *M* nitrogen compound (= *A*) + *b* ml supplements + ad 20 ml (or 10 ml) H_2O + *x* ml m*M* sodium-tetraphenylboron (TPB) T = 20°

Expt. No.	*Solution of nitrogen compound*	*Initial ppt. at ml*	*Vol. ml*	*Titrant (= TPB)*			*Optical density at the end-point*	*Molar ratio [A]:[TPB]*	*% error*	*Titration time in min*	*Intermediate compounds*
				Molarity	*End-point (ml)*						
					Calcul.	*Found*					
1	3 ml 0.001 *M* acriflavine + 1 ml *N* HCl	0.1	20	0.001	3.00	i 3.00 h	0.72	1 : 1	0.0	25	3 : 2↓
2	3 ml 0.001 *M* acriflavine + 1 ml *M* Na-acetate	0.1	20	0.001	3.00	i 3.00 h	0.8	1 : 1	0.0	22	2 : 1↓
3	3 ml 0.001 *M* acriflavine + 5 ml 0.2 *M* Na_2HPO_4	0.1	20	0.001	3.00	i 3.00 h	0.66	1 : 1	0.0	25	2 : 1↓
4	4 ml 0.001 *M* rivanol + 1 ml *N* HCl	1.0	20	0.001	4.00	i 4.00 h	0.57	1 : 1	0.0	28	4 : 1↑
5	4 ml 0.001 *M* rivanol + 1 ml *M* Na-acetate	1.0	20	0.001	4.00	i 4.00 h	0.62	1 : 1	0.0	29	4 : 1↑
6	4 ml 0.001 *M* rivanol + 5 ml 0.2 *M* Na_2HPO_4	1.2	20	0.001	4.00	i 4.00 h	0.54	1 : 1	0.0	38	4 : 1↑
7	4 ml 0.001 *M* nitron + 1 ml *N* HCl	0.1	20	0.001	4.00	i 4.00 h	0.79	1 : 1	0.0	12	
8	4 ml 0.001 *M* nitron + 2 ml *N* CH_3COOH	0.1	20	0.001	4.00	i 3.99 h	0.82	1 : 1	0.2	11	
9	4 ml 0.001 *M* nitron + 2 ml *M* Na-acetate	0.1	20	0.001	4.00	i 4.00 h	0.80	1 : 1	0.0	11	
10	4 ml 0.001 *M* nitron + 5 ml 0.2 *M* Na_2HPO_4	0.1	20	0.001	4.00	i 3.98 h	0.74	1 : 1	0.5	12	
11	4 ml 0.001 *M* cinchonine + 1 ml *N* HCl	0.3	20	0.0025	3.20	i 3.20 h	0.73	1 : 2	0.0	14	1 : 1↓ → 2 : 3↓
12	4 ml 0.001 *M* cinchonine + 2 ml *N* CH_3COOH	0.3	20	0.0025	3.20	i 3.18 h	0.86	1 : 2	0.5	14	1 : 1↓ → 2 : 3↓
13	4 ml 0.001 *M* cinchonine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.3	20	0.0025	3.20	i 3.20 h	0.81	1 : 2	0.0	13	1 : 1↓ → 2 : 3↓
14	6 ml 0.001 *M* cinchonine + 2 ml *M* Na-acetate	0.1	20	0.0025	3.60	i 3.58 h	0.89	2 : 3	0.5	16	3 : 2↓ → 1 : 1↓
15	6 ml 0.001 *M* cinchonine + 5 ml 0.2 *M* Na_2HPO_4	0.1	20	0.0025	3.60	i 3.60 h	0.88	2 : 3	0.0	16	3 : 2↓ → 1 : 1↓
16	5 ml 0.001 *M* quinine + 1 ml *N* HCl	1.0	20	0.0025	4.00	i 4.00 h	0.95	1 : 2	0.0	11	2 : 1↑ → 1 : 1↓ → 2 : 3↓
17	5 ml 0.001 *M* quinine + 2 ml *N* CH_3COOH	0.3	20	0.0025	4.00	i 4.00 h	1.01	1 : 2	0.0	11	1 : 1↓
18	5 ml 0.001 *M* quinine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.2	20	0.0025	4.00	i 3.98 h	0.90	1 : 2	0.5	12	1 : 1↓

19	5 ml 0.001 *M* quinine + 2 ml *M* Na-acetate	0.3	20	0.0025	3.00	i 3.00 h	0.79	2 : 3	0.0	13	3 : 2↓ → 1 : 1↓
20	5 ml 0.001 *M* quinine + 5 ml 0.2 *M* Na_2HPO_4	0.4	20	0.0025	3.00	i 3.00 h	0.70	2 : 3	0.0	13	3 : 2↓ → 1 : 1↓
21	5 ml 0.001 *M* strychnine + 1 ml *N* HCl	0.4	20	0.00133	3.75	i 3.72 h	0.67	1 : 1	1.0	32	~2 : 1↓ → 3 : 2↓
22	5 ml 0.001 *M* strychnine + 2 ml *N* CH_3COOH	0.3	20	0.00133	3.75	i 3.80 h	0.74	1 : 1	1.0	32	~2 : 1↓ → 4 : 3↓
23	5 ml 0.001 *M* strychnine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.4	20	0.00133	3.75	i 3.75 h	0.70	1 : 1	0.0	29	~2 : 1↓ → 4 : 3↓
24	5 ml 0.001 *M* strychnine + 2 ml *M* Na-acetate	0.4	20	0.00133	3.75	i 3.82 h	0.61	1 : 1	1.4	30	3 : 1↓ → 2 : 1↓
25	5 ml 0.001 *M* strychnine + 5 ml 0.2 *M* Na_2HPO_4	1.2	20	0.00133	3.75	i 3.78 h	0.35	1 : 1	0.5	33	~4 : 1↑ → 2 : 1↓
26	5 ml 0.001 *M* papaverine + 1 ml *N* HCl	0.1	20	0.0015	3.33	i 3.38 h	0.73	1 : 1	1.4	16	3 : 1↓ → ~3 : 2↓ (?)
27	5 ml 0.001 *M* papaverine + 2 ml *N* CH_3COOH	0.1	20	0.0015	3.33	i 3.36 h	0.88	1 : 1	0.8	17	2 : 1↓ → 3 : 2↓
28	5 ml 0.001 *M* papaverine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.1	20	0.0015	3.33	i 3.33 h	0.81	1 : 1	0.0	16	2 : 1↓ → ~3 : 2↓
29	5 ml 0.001 *M* papaverine + 2 ml *M* Na-acetate	0.1	20	0.0015	3.33	i 3.37 h	0.82	1 : 1	1.2	17	3 : 1↓ → 2 : 1↓ → 3 : 2↓
30	5 ml 0.001 *M* sparteine + 1 ml *N* HCl	1.1	20	0.0025	4.00	i 4.00 h	0.62	1 : 2	0.0	17	2 : 1↑ → (1 : 1↓)
31	6 ml 0.001 *M* sparteine + 2 ml *N* CH_3COOH	0.1	20	0.0015	4.00	i 4.00 h	0.73	1 : 1	0.0	16	2 : 1↓ → 3 : 2↓
32	6 ml 0.001 *M* sparteine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.1	20	0.0015	4.00	i 4.00 h	0.74	1 : 1	0.0	16	4 : 3↓
33	6 ml 0.001 *M* sparteine + 2 ml *M* Na-acetate	0.1	20	0.0015	4.00	i 4.00 h	0.74	1 : 1	0.0	16	2 : 1↓ → ~4 : 3↓
34	6 ml 0.001 *M* sparteine + 5 ml 0.2 *M* Na_2HPO_4	0.1	20	0.0015	4.00	i 4.00 h	0.82	1 : 1	0.0	17	~3 : 1↓ → ~3 : 2↓
35	7 ml 0.001 *M* phenanthroline + 1 ml *N* HCl	0.1	20	0.002	3.50	i 3.50 h	0.86	1 : 1	0.0	11	~2 : 1↓ → 3 : 2↓
36	7 ml 0.001 *M* phenanthroline + 2 ml *N* CH_3COOH	0.1	20	0.002	3.50	i 3.50 h	0.90	1 : 1	0.0	11	~2 : 1↓ → 3 : 2↓
37	7 ml 0.001 *M* phenanthroline + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.1	20	0.002	3.50	i 3.50 h	0.74	1 : 1	0.0	12	3 : 1↓ → 2 : 1↓ → 3 : 2↓
38	7 ml 0.001 *M* phenanthroline + 2 ml *M* Na-acetate		20	0.002		no ppt.					

continued

TABLE I (continued)

Expt. No.	Solution of nitrogen compound	Initial ppt. at ml	Vol. ml	Titrant (= TPB)			Optical density at the end-point	Molar ratio [A]:[TPB]	% error	Titration time in min	Intermediate compounds
				Molarity	End-point (ml)						
					Calcul.	Found					
39	3 ml 0.005 *M* pyramidone + 1 ml *N* HCl	0.4	10	0.005	3.00	i 3.00 h	0.80	1 : 1	0.0	26	2 : 1↓
40	3 ml 0.005 *M* pyramidone + 2 ml *N* CH_3COOH	0.5	10	0.005	3.00	i 3.00 h	0.97	1 : 1	0.0	25	2 : 1↓ → 3 : 2↓
41	3 ml 0.005 *M* pyramidone + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.4	10	0.005	3.00	i 3.00 h	0.85	1 : 1	0.0	23	2 : 1↓ → 3 : 2↓
42	3 ml 0.005 *M* pyramidone + 2 ml *M* Na-acetate		10	0.005		no ppt.					
43	3 ml 0.005 *M* antipyrine + 1 ml *N* HCl		10	0.0025	3.00	i 3.00 h	0.69	2 : 1	0.0	17	3 : 1↓
44	3 ml 0.005 *M* antipyrine + 5 ml *N* HCl	0.2	10	0.0025	3.00	i 3.00 h	0.64	2 : 1	0.0	14	5 : 1↓ → 3 : 1↓
45	3 ml 0.005 *M* antipyrine + 2 ml *N* CH_3COOH	0.6	10	0.0025	3.00	i 3.00 h	0.40	2 : 1	0.0	19	3 : 1↓
46	3 ml 0.005 *M* antipyrine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate					no ppt.					
47	4 ml 0.004 *M* atropine + 1 ml *N* HCl	0.6	20	0.004	4.00	i 3.97 h	0.60	1 : 1	0.8	10	<3 : 2↓ → 4 : 3↓
48	4 ml 0.004 *M* atropine + 2 ml *N* CH_3COOH	0.7	20	0.004	4.00	i 4.00 h	0.72	1 : 1	0.0	10	2 : 1↓ → ~4 : 3↓
49	4 ml 0.004 *M* atropine + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	0.7	20	0.004	4.00	i 4.01 h	0.95	1 : 1	0.2	7	2 : 1↓ → 3 : 2↓
50	4 ml 0.004 *M* atropine + 2 ml *M* Na-acetate	0.6	20	0.004	4.00	i 4.00 h	0.92	1 : 1	0.0	10	<2 : 1↓ → 4 : 3↓
51	4 ml 0.004 *M* atropine + 5 ml 0.2 *M* Na_2HPO_4	0.7	20	0.004	4.00	i 4.00 h	0.94	1 : 1	0.0	8	<2 : 1↓ → 3 : 2↓
52	4 ml 0.01 *M* oxine + 1 ml *N* HCl	0.5	10	0.005	4.00	i 4.00 h	0.74	2 : 1	0.0	14	~6 : 1↓ → ~4 : 1↓ → 3 : 1↓
53	4 ml 0.01 *M* oxine + 2 ml *M* Na-acetate	0.2	10	0.005	4.00	i 4.00 sh. h	0.34	2 : 1	0.0	10	~8 : 1↑ → ~4 : 1↓ → 3 : 1↓

i = intersection point; h = horizontal maximum density line; ↑ = soluble intermediate; ↓ = insoluble intermediate; ↓↓ = final compound at the first optical maximum density point.

The striking difference in sensitivity towards each titrant in the case of acriflavine and rivanol must be caused by the "ribboned" structure of these compounds when acting as cations. Generally the sensitivity of the titrations with TPB is only a third of that with bismuth iodide. But in the case of acriflavine and rivanol, almost equal amounts of compound were required for the analysis in each cases. Although the sensitivities with TPB and bismuth iodide were different, the compounds could be determined with both reagents with the same precision; the error was usually zero. Generally the titration time was about twice as long with TPB as with bismuth iodide.

COMPOUNDS

Final compounds

Probably all the final compounds obtained in this work are composed of large regular salts without complex formation. *Four* final compounds were obtained:

$$A_2[TPB]\downarrow\downarrow,\ A[TPB]\downarrow\downarrow,\ A_2[TPB]_3\downarrow\downarrow \text{ and } A[TPB]_2\downarrow\downarrow.$$

In all titrations the first maximum density point coincided exactly with the quantitative formation of one of these compounds. Therefore, all the above compounds could be used equally successfully for the analysis of the nitrogen-containing compounds. The following may be stated regarding the composition of the final compound. The compound $A[TPB]_2\downarrow\downarrow$ was only obtained at pH values of 1–5 with two alkaloids, namely, quinine and cinchonine. Both these compounds contain two ring systems with one nitrogen in each ring. The N-atoms lie apart from each another and act separately and independently.

In addition, sparteine (Table I, Expt. 30 and Table II, Expts. 11 and 12) also gave a final compound $A[TPB]_2\downarrow\downarrow$ at low pH values. With bismuth iodide, the activity of the N-atoms was more pronounced. Thus, both nitron and antipyrine gave final compounds $A[BiI_n]_2\downarrow\downarrow$ if titrated with bismuth. But if titrated with TPB, the second nitrogen always remained inactive. In the reverse titrations of bismuth iodide with nitron, only one nitrogen was used in the titration and the final compound $A[BiI_n]\downarrow\downarrow$ was obtained, just as in all titrations with TPB, $A[TPB]\downarrow\downarrow$ was obtained. Thus parallel heterometric titrations with both titrants may reveal fine differences in the electronic and the stereochemical structure of the complex cyclic nitrogen compound.

In two cases, the composition of the final compounds depended on the pH value of the titrated solution, *i.e.* with cinchonine and quinine (Table I, Expts. 11–20 and Table II, Expts. 19–28). The compound $A_2[TPB]_3\downarrow\downarrow$ obtained in both cases at pH values 7–9 must be considered as having the structure of a stoechiometric mixture of $A[TPB] + A[TPB]_2\downarrow\downarrow$.

The final compound $A_2[TPB]\downarrow\downarrow$ obtained with antipyrine and with oxine (Table I, Expts. 43–46, 52–53 and Table II, Expts. 32–34, 49) presents a special problem. In the reverse titration oxine also gave a final compound $A[TPB]\downarrow\downarrow$ at pH value ~ 1, (Table II, Expt. 48), while antipyrine always gave the compound $A_2[TPB]\downarrow\downarrow$ only. It is hardly conceivable that TPB can act as a doubly charged anion $[TPB]^{-2}$. On the other hand, the assumption that with both the latter nitrogen compounds an additional molecule of the compound was necessary for the formation of the solid compound is not readily comprehensible. It is interesting to note that each of these compounds contains two attraction points in the molecule, *i.e.* either two N-atoms

TABLE II

General composition: *a* ml K*M* tetraphenylboron (TPB) + *b* ml supplements + ad 20 ml (or 10 ml) water + *x* ml m*M* N-compound (= A)T = 20°

Expt. No.	*Solution titrated*	*Vol. ml*	*Initial ppt. at ml*	*Titrant (= A)*				*Optical density at the end-point*	*Molar ratio [A]:[TPB]*	*% error*	*Titration time in min*	*Intermediate compounds*
				Name	*Molarity*	*End-point*						
						Calcul.	*Found*					
1	3 ml 0.001 *M* TPB + 1 ml *N* HCl	20	0.1	Acriflavine	0.001	3.0	i 3.0 h	0.79	1 : 1	0.0	33	1 : 3↓
2	3 ml 0.001 *M* TPB + 2 ml *N* CH_3COOH	20	0.1	Acriflavine	0.001	3.0	i 3.0 h	0.78	1 : 1	0.0	20	
3	3 ml 0.001 *M* TPB + 2 ml *M* Na-acetate	20	0.1	Acriflavine	0.001	3.0	i 3.0 h	0.62	1 : 1	0.0	24	
4	4 ml 0.001 *M* TPB + 1 ml *N* HCl	20	0.1	Nitron	0.001	4.0	i 4.00 h	0.79	1 : 1	0.0	11	
5	4 ml 0.001 *M* TPB + 2 ml *N* CH_3COOH	20	0.1	Nitron	0.001	4.0	i 4.01 h	0.98	1 : 1	0.2	13	
6	4 ml 0.001 *M* TPB + 2 ml *M* Na-acetate	20	0.1	Nitron	0.001	4.0	i 4.02 h	0.90	1 : 1	0.5	12	
7	4 ml 0.001 *M* TPB + 5 ml 0.2 *M* Na_2HPO_4	20	0.1	Nitron	0.001	4.0	i 4.01 h	0.84	1 : 1	0.2	13	
8	4 ml 0.001 *M* TPB + 1 ml *N* HCl	20	0.1	Papaverine	0.001	4.0	i 4.00 h	0.82	1 : 1	0.0	18	1 : 2↓ → 2 : 3↓
9	4 ml 0.001 *M* TPB + 2 ml *N* CH_3COOH	20	0.1	Papaverine	0.001	4.0	i 4.02 h	0.88	1 : 1	0.5	18	1 : 2↓ → 2 : 3↓
10	4 ml 0.001 *M* TPB + 2ml *M* Na-acetate	20	0.2	Papaverine	0.001	4.0	i 4.02 h	0.83	1 : 1	0.5	19	1 : 2↓ → 2 : 3↓
11	8 ml 0.0025 *M* TPB + 1 ml *N* HCl	20	0.0	Sparteine	0.0025	4.0	i 4.00 h	0.77	1 : 2	0.0	14	(1 : 8↓) → 1 : 6↓ → 1 : 4↓
12	4 ml 0.0025 *M* TPB + 1 ml *N* HCl	20	2.0	Sparteine	0.00125	4.0	i 4.00 h	0.21	1 : 2	0.0	22	1 : 4↑ → ~1 : 3↓
13	4 ml 0.0015 *M* TPB + 2 ml *N* CH_3COOH	20	0.3	Sparteine	0.0015	4.0	i 4.02 h	0.78	1 : 1	0.5	15	1 : 2↓
14	4 ml 0.0015 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	20	0.1	Sparteine	0.0015	4.0	i 4.00 h	0.89	1 : 1	0.0	16	1 : 2↓ → 3 : 4↓
15	4 ml 0.0015 *M* TPB + 2 ml *M* Na-acetate	20	0.1	Sparteine	0.0015	4.0	i 4.00 h	0.90	1 : 1	0.0	16	1 : 2↓ → 3 : 4↓
16	4 ml 0.0015 *M* TPB + 5 ml 0.2 *M* Na_2HPO_4	20	0.1	Sparteine	0.0015	4.0	i 4.00 h	0.93	1 : 1	0.0	17	1 : 2↓ → 3 : 4↓
17	3 ml 0.002 *M* TPB + 1 ml *N* HCl	20	0.1	Rivanol	0.002	3.0	i 3.00 h	0.88	1 : 1	0.0	38	1 : 3↓ → 2 : 3↓
18	3 ml 0.002 *M* TPB + 2 ml *M* Na-acetate	20	0.1	Rivanol	0.002	3.0	i 3.00 h	0.95	1 : 1	0.0	40	2 : 3↓
19	3 ml 0.0025 *M* TPB + 1 ml *N* HCl	20	0.2	Quinine	0.001	3.75	i 3.8 h	0.84	1 : 2	1.3	12	~1 : 8↓ → 1 : 4↓
20	3 ml 0.0025 *M* TPB + 2 ml *N* CH_3COOH	20	0.2	Quinine	0.001	3.75	i 3.8 h	0.90	1 : 2	1.3	12	1 : 4↓
21	3 ml 0.0025 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	20	0.2	Quinine	0.001	3.75	i 3.8 h	0.75	1 : 2	1.3	12	1 : 4↓ → 1 : 3↓
22	5 ml 0.00125 *M* TPB + 2 ml *M* Na-acetate	20	1.0	Quinine	0.001	4.16	i 4.2 h	0.52	2 : 3	1.0	18	1 : 6↑ → 1 : 3↓ → 1 : 2↓
23	5 ml 0.00125 *M* TPB + 5 ml 0.2 *M* Na_2HPO_4	20	0.9	Quinine	0.001	4.16	i 4.2 h	0.54	2 : 3	1.0	20	1 : 6↑ → 1 : 3↓ → 1 : 2↓
24	6 ml 0.00125 *M* TPB + 1 ml *N* HCl	20	0.1	Cinchonine	0.001	3.75	i 3.80 h	0.59	1 : 2	1.3	14	1 : 4↓
25	6 ml 0.00125 *M* TPB + 2 ml *N* CH_3COOH	20	0.1	Cinchonine	0.001	3.75	i 3.80 h	0.93	1 : 2	1.3	14	~1 : 3↓

26	6 ml 0.00125 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	20	0.1	Cinchonine	0.001	3.75	i 3.80	h 0.66	1 : 2	1.3	13	1 : 4↓
27	5 ml 0.00125 *M* TPE + 2 ml *M* Na-acetate	20	0.6	Cinchonine	0.001	4.16	i 4.20	h 0.64	2 : 3	1.0	17	1 : 4↓ → 1 : 3↓ → 1 : 2↓
28	5 ml 0.00125 *M* TPB + 5 ml 0.2 *M* Na_2HPO_4	20	1.1	Cinchonine	0.001	4.16	i 4.18	h 0.36	2 : 3	0.5	17	1 : 6↑ → ~1 : 4↓ → 1 : 2↓
29	7.5 ml 0.001 *M* TPB + 1 ml *N* HCl	20	0.2	Strychnine	0.002	3.75	i 3.8	h 0.94	1 : 1	1.3	48	1 : 2↓ → 2 : 3↓
30	7.5 ml 0.001 *M* TPB + 2 m *N* CH_3COOH + + 2 ml *M* Na-acetate	20	0.1	Strychnine	0.0025	3.0	i 3.0	h 0.95	1 : 1	0.0	52	1 : 2↓ → 2 : 3↓
31	10 ml 0.001 *M* TPB + 5 ml 0.2 *M* Na_2HPO_4	20	0.3	Strychnine	0.0033	3.33	i 3.38	h 0.85	1 : 1	1.3	52	~1 : 2↓
32	3 ml 0.0025 *M* TPB + 1 ml *N* HCl	10	0.1	Antipyrine	0.005	3.0	i 3.00	h 0.84	2 : 1	0.0	20	1 : 1↓
33	3 ml 0.0025 *M* TPB + 2 ml *N* CH_3COOH	10	1.4	Antipyrine	0.005	3.0	i 3.00	h 0.43	2 : 1	0.0	22	1 : 1↑
34	3 ml 0.0025 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	10		Antipyrine	0.005		no ppt.					
35	4 ml 0.002 *M* TPB + 1 ml *N* HCl	20	0.1	Phenanthroline	0.002	4.0	i 4.00	h 0.87	1 : 1	0.0	13	1 : 4↓ → 1 : 2↓ → 3 : 4↓
36	4 ml 0.002 *M* TPB + 2 ml *N* CH_3COOH	20	0.1	Phenanthroline	0.002	4.0	i 4.00	h 1.03	1 : 1	0.0	12	1 : 4↓ → 2 : 3↓
37	4 ml 0.002 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	20	0.1	Phenanthroline	0.002	4.0	i 4.00	h 0.83	1 : 1	0.0	12	1 : 4↓ → 1 : 2↓ → 2 : 3↓
38	4 ml 0.002 *M* TPB + 2 ml *M* Na-acetate	20		Phenanthroline	0.002		no ppt.					
39	3 ml 0.005 *M* TPB + 1 ml *N* HCl	10	0.4	Pyramidon	0.005	3.0	i 3.0	h 0.88	1 : 1	0.0	22	1 : 3↓
40	3 ml 0.005 *M* TPB + 2 ml *N* CH_3COOH	10	0.4	Pyramidon	0.005	3.0	i 3.0	h 0.95	1 : 1	0.0	23	1 : 3↓ → 1 : 2↓
41	3 ml 0.005 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	10	0.5	Pyramidon	0.005	3.0	i 3.0	h 0.70	1 : 1	0.0	20	1 : 3↓ → 1 : 2↓
42	3 ml 0.005 *M* PTB + 2 ml *M* Na-acetate	10		Pyramidon	0.005		no ppt.					
43	4 ml 0.004 *M* TPB + 1 ml *N* HCl	20	0.8	Atropine	0.004	4.0	i 4.00	h 0.79	1 : 1	0.0	9	3 : 4↓
44	4 ml 0.004 *M* TPB + 2 ml *N* CH_3COOH	20	0.7	Atropine	0.004	4.0	i 4.00	h 0.92	1 : 1	0.0	9	1 : 2↓ → 2 : 3↓
45	4 ml 0.004 *M* TPB + 2 ml *N* CH_3COOH + + 2 ml *M* Na-acetate	20	0.9	Atropine	0.004	4.0	i 4.00	h 0.84	1 : 1	0.0	8	~1 : 4↑ → 3 : 4↓
46	4 ml 0.004 *M* TPB + 2 ml *M* Na-acetate	20	0.8	Atropine	0.004	4.0	i 4.00	h 0.82	1 : 1	0.0	8	~1 : 4↑ → 2 : 3↓
47	4 ml 0.004 *M* TPB + 5 ml 0.2 *M* Na_2HPO_4	20	0.8	Atropine	0.004	4.0	i 4.00	h 0.77	1 : 1	0.0	8	~1 : 4↑ → 1 : 2↓ → 2 : 3↓
48	4 ml 0.005 *M* TPB + 1 ml *N* HCl	10	0.5	Oxine	0.01	2.00	i 2.00	h 0.62	1 : 1	0.0	12	1 : 4↑ → 1 : 2↓ → 3 : 4↓
49	4 ml 0.01 *M* TPB + 2 ml *M* Na-acetate	10	0.6	Oxine	0.02	4.00	i 4.00	h 0.59	2 : 1	0.0	16	1 : 4↑ → 1 : 1↓ → 3 : 2↓

i = intersection point; h = horizontal maximum density line; ↑ = soluble intermediate; ↓ = insoluble intermediate; ↓↓ = final compound at the first optical maximum density point.

or one N-atom and one OH-group. In other studies with TPB we have found intermediates in which the [TPB]⁻ acted with four attraction points; the latter may only be the four phenyl groups. If so, both the stereochemical and the electronic moments are responsible for the formation of the stable final compound A_2[TPB]↓↓.

It is interesting to note that CRANE[2], who also analysed the compound formed between TPB and oxine, found the bimolecular compound A_2[TPB] only.

Because of the reduced sensitivity of TPB towards N-atoms, the final compound A[TPB]↓↓ with one active nitrogen atom was usually obtained in this work. This was also the case when nitron, pyramidone, phenanthroline or atropine was titrated with TPB.

In contrast to the reaction between nitrogen-containing compounds and bismuth iodide, final compounds of the same composition were obtained in all titrations whether the compounds were titrated with TPB or vice versa. Oxine was the only exception, giving in the reverse titrations A[TPB]↓↓ at pH ∿1, and A_2[TPB]↓↓ at pH ∿7.

Intermediate compounds

The different sequences of intermediate compounds traced depended on the final compounds obtained. The sequences were different in straight titrations of alkaloids with TPB and in the reverse titrations.

Thus the following sequences of intermediate compounds, at the molar ratio of [A] : [TPB], were obtained if the nitrogen compounds were titrated with TPB:

(1) 4 : 1↑ → 3 : 1↓↑* → 2 : 1↓↑ → 3 : 2↓ → 1 : 1↓↓
(2) 1 : 1↓ → 2 : 3↓ → 1 : 2↓↓ (pH's 1–5)
(3) 3 : 2↓ → 1 : 1↓ → 2 : 3↓↓ (pH's 7–9)
(4) 4 : 1↓ → 3 : 1↓ → 2 : 1↓↓

In the reverse titrations of TPB with alkaloids, the following sequences of compounds at the molar ratio of [A] : [TPB] were obtained:

(5) (1 : 4↓) → 1 : 2↓ → 2 : 3↓ → 1 : 1↓↓
(6) (1 : 6↓) → 1 : 4↓ → 1 : 2↓↓ (pH's 1–5)
(7) 1 : 6↓ → 1 : 3↓ → 1 : 2↓ → 2 : 3↓↓ (pH's 7–9)
(8) 1 : 1↓ → 3 : 2↓ → 2 : 1↓↓

The pH dependence of the reactions

With the exception of cinchonine and quinine, the same final compounds were obtained at all pH values between ∿1 and ∿9. This is very striking, as it must be assumed that the nitrogen compounds always acted as cations. Generally the highest maximum density values were obtained at pH ∿3. In some cases the high pH values acted favourably on the maximum density values obtained (*e.g.* cinchonine, sparteine and atropine). In other cases, there was an optimum pH value above which the maximum density value decreased gradually with rising pH (*e.g.* acriflavine, rivanol. quinine, strychnine, phenanthroline, antipyrine and oxine).

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* ↓↑ = the compound may be either insoluble or soluble.

No precipitation at all occurred at pH ∿5 with antipyrine or at pH ∿7 with phenanthroline or pyramidone. The sensitivity of the precipitation towards increase in pH was very pronounced in ring compounds containing two nitrogen atoms bound to one another (*e.g.* pyramidone and antipyrine) or two nitrogen atoms stereochemically near one another (*e.g.* phenanthroline).

The pH of the solution probably plays a double role; low pH values favour the function of the N-atoms as cations, but also increase the solubility of the large salt. If so, the most basic compounds should give the best results at higher pH values. Two N-atoms in close vicinity weaken the basic character of the compound and make it more sensitive to rising pH values and more soluble.

ANALYTICAL ASPECTS

TPB is about three times less sensitive towards large nitrogen-containing compounds than bismuth as iodide, but it is possible to carry out titrations at pH values of 1–9. Because of the solubility of TPB this reagent can be used in any desired concentration. TPB can thus be used for the determination, or for the study, of less sensitive compounds, which was impossible with bismuth. Less complex molecules such as hexamethylenetetramine, caffeine, etc. can be studied with TPB in larger concentrations. On the other hand, the sensitivity towards TPB is high in special cases such as the "ribboned" acriflavine or rivanol. At pH ∿7 complex nitrogen compounds can be studied and analysed in the presence of bi- or polyvalent metals, which can be kept in solution by the addition of masking agents. All these aspects will be considered in future reports, more nitrogen compounds will be included and single compounds will be determined in mixtures. The following may be stated regarding the sensitivity of the determinations with TPB. Approximately one mg of compound in 20 ml of solution was necessary for the determination of the most sensitive compounds such as acriflavine, nitron, cinchonine and phenanthroline. About two mg were necessary in the case of quinine, strychnine, papaverine and sparteine. About double the amount was necessary in the case of the less sensitive alkaloids such as antipyrine and atropine. These latter remained in solution when the titration was carried out at pH ∿7, and thus the determination could be extended to mixtures.

GENERAL METHOD

1–2 mg of the large nitrogen-containing compound in 20 ml of aqueous solution, containing 2 ml of *N* acetic acid (or 1 ml of *N* hydrochloric acid) are titrated with a 0.001–0.005 *M* aqueous solution of sodium tetraphenylboron.

Note: In the case of smaller compounds the amount of sample and the concentration of the TPB must be increased.

SUMMARY

The reactions between tetraphenylboron (TPB) and acriflavine, rivanol, nitron, cinchonine, quinine, strychnine, papaverine, sparteine, phenanthroline, pyramidon, antipyrine, atropine and oxine were studied heterometrically at pH values 1–9. The reactions were about one third as sensitive as with bismuth nitrate in iodide solution. The sensitivity in the above series decreases from acriflavine to oxine. Precise titrations could always be carried out with TPB. Compounds with two adjacent N-atoms gave no precipitation at pH 5–7. The structures of the compounds and the analytical aspects are discussed and a method of determination is presented.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique des réactions entre l'anion tétraphénylborique et les composés suivants: acriflavine, rivanol, nitron, cinchonine, quinine, strychnine, papavérine, spartéine, phénanthroline, pyramidon, antipyrine, atropine et oxine. La structure des composés obtenus est discutée; une méthode de dosage est proposée.

ZUSAMMENFASSUNG

Die Reaktionen des Tetraphenylbor-anions mit Acriflavin, Rivanol, Nitron, Cinchonin, Chinin, Strychnin, Papaverin, Spartein, Phenanthrolin, Pyramidon, Antipyrin, Atropin und Oxin wurden heterometrisch untersucht. Die Strukturen der Reaktionsprodukte werden diskutiert und eine Methode zur Bestimmung dieser Verbindungen beschrieben.

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INFRARED DETERMINATION OF TRACES OF SULFATE IN REAGENT CHEMICALS

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Although the infrared spectra of a large number of inorganic compounds have accumulated in the literature, there have been relatively few applications of infrared spectrophotometry to inorganic analytical problems. This is partly because of the solvent problem, but the alkali halide pressed disk technique[1-3], coupled with freeze-drying[4,5] actually makes it relatively easy to obtain the infrared spectra of materials present originally in aqueous solution. It is particularly interesting to consider the possibility of developing infrared methods for the determination of small quantities of inorganic anions because it is precisely in this area that other modern analytical techniques have been most deficient. An investigation of the infrared spectrophotometry of the sulfate ion was reported recently[5] which emphasized the techniques and results but did not deal with applications. In this paper, it is shown that these techniques can be combined with a chromatographic concentration and isolation step to provide a method for determining small quantities of sulfate in samples containing massive quantities of other substances. The method is well suited to the determination of sulfate impurities in reagent chemicals. It is as accurate as is ordinarily required at the trace level, and while it is not rapid from the standpoint of total elapsed time, it requires a very small amount of operator time per sample because a large number of samples can be processed together with a minimum of attention.

SCHWAB AND DATTLER[6] were apparently the first to observe the retention of anions on columns of acid-washed alumina, and they worked out a selectivity series for about a dozen anions. KUBLI[7] later added a few more ions to the series. Sulfate stood high in its tendency to be retained but was easily displaced by hydroxyl ion. NYDAHL[8,9] then showed that analytical separations of sulfate from many other anions were feasible in practice, and developed methods for sulfur in steels, biological materials, and other types of samples, in which the chromatographic separation of sulfate on alumina was the key step. In addition, he measured distribution coefficients for sulfate and several other anions under various conditions, pointed out the important effect of pH upon sulfate retention, and emphasized that alumina was very much more selective for sulfate than were synthetic anion-exchange resins. FRITZ *et al.*[10] studied the process further in developing a separation designed to precede a titrimetric sulfate determination, and noted the remarkable facts that sulfate was quantitatively adsorbed even from 5 M perchloric acid or 2 N hydrochloric acid solutions, even at dilutions as low as 0.5 p.p.m., and even at ratios of chloride to sulfate of at least 4500 : 1. At the same time, it was relatively easy to elute the sulfate at will by means of hydroxyl ion, *e.g.*, with a dilute ammonia solution.

It was reasonable to try to combine this excellent separation technique with the infrared determination of sulfate. The coupling occurs through the freeze-drying step: potassium bromide is added to the column eluate, the solution is freeze-dried, and the resulting powder is pressed into a disk for infrared examination. The column operation takes only a few minutes, and the disk pressing and infrared recording likewise are not time-consuming. The freeze-drying operation unfortunately is slow, but once set in operation, it requires no attention. The work can conveniently be planned so that samples freeze-dry overnight. Furthermore, as many samples as desired can be freeze-dried at one time. Thus in practice the method is fairly rapid in terms of operator time per sample.

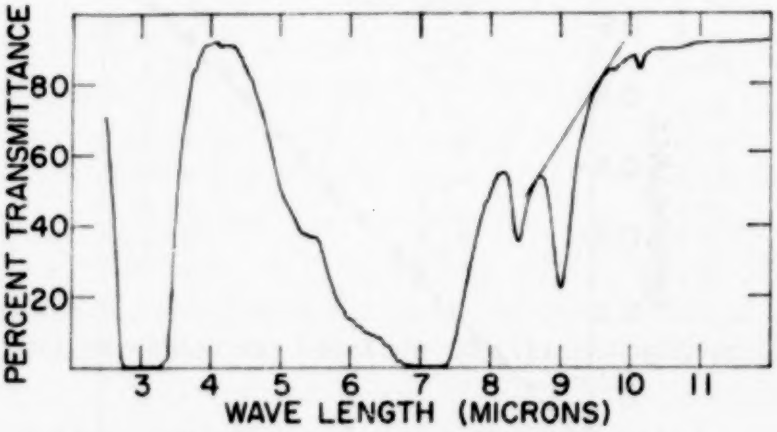

Fig. 1. Spectrum of freeze-dried column eluate.

In the previous report[5], it was noted that the shape and intensity of the sulfate band near 9μ varied with the cation accompanying the sulfate, and potassium sulfate was recommended as best for quantitative measurements. However, the sulfate in the column eluate appears as ammonium sulfate if, as seems best, ammonia is the eluting agent. The spectrum of a freeze-dried column eluate is shown in Fig. 1. This spectrum is not so good as that of potassium sulfate because it is more difficult to establish the base-line, but experience has shown that reliable results can be obtained using a base-line like that indicated in the figure. Preliminary attempts to convert the column eluate into potassium sulfate by means of ion-exchange columns were unsuccessful because, although the cation exchange of potassium for ammonium did occur, extraneous absorption bands, some of which interfered with the sulfate band, were introduced by the action of the ammoniacal solution upon the resins. No amount of prior washing of the resins prevented this.

EXPERIMENTAL

Apparatus and reagents

Infrared spectra were recorded with a Perkin-Elmer Model 137 "Infracord" spectrophotometer. Only the spectrum from about 7 to 11 μ was required. Solutions were freeze-dried in tubes about 10 cm long made from standard taper 19/38 inner joints, using a 24-port VirTis freeze-dryer. Disks were prepared with a Hilger H920 die obtained from the Jarrell-Ash Co., Newtonville, Mass., using a Loomis 20-ton hydraulic press.

The chromatographic column was similar to those described by NYDAHL[9] and FRITZ[10], about 10 cm long and 1 cm in diameter. The treatment of the alumina has also been described[9,10]. The alumina used in this work was Alcoa activated alumina, grade F-20; this material was free of elutable sulfate, whereas some samples of chromatographic alumina from other sources contained large quantities of sulfate which slowly came off the column for an indefinite time.

A special grade of potassium bromide for infrared work, manufactured by E. Merck, Darmstadt, Germany, was obtained from Terra Chemicals, Inc., New York, N.Y. Ordinary reagent-grade potassium bromide often shows a very slight absorption in the sulfate region, whereas the E. Merck preparation does not. All other chemicals used were of the usual reagent-grade; the principal ones, hydrochloric acid and ammonia, fortunately were found to be sulfate-free.

Preliminary experiments

Since ammonium sulfate is not a suitable standard material, a calibration curve was prepared based upon oven-dried potassium sulfate. Aliquots of a standard solution were run through the entire procedure including the chromatographic step (see procedure below) to yield the data shown in Fig. 2. This calibration curve appears to be reproducible but of course it is good practice to run standards through the procedure along with each batch of unknown samples.

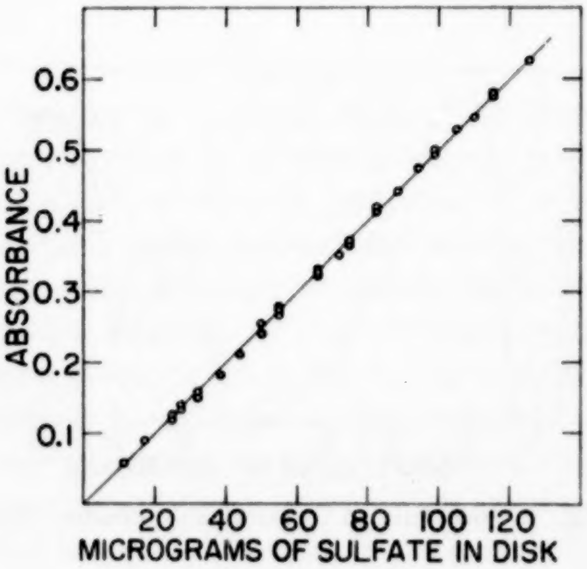

Fig. 2. Calibration curve.

Because the potassium bromide which was on hand was known to be sulfate-free, it was the first salt to be studied for interference in the procedure. It was found, in the most extreme case tested, that bromide in weight ratio to sulfate of 12,000 : 1 did not interfere in any way. According to KUBLI's selectivity series[7], chloride, nitrate, permanganate, perchlorate, acetate and sulfide are all less strongly retained on alumina than is bromide, and hence interference from these ions would not be expected. Iodide, nitrite and thiocyanate are held only slightly more strongly than bromide and likewise could be tolerated in fairly large amounts.

It was believed that phosphate might be the most troublesome ion because it is often present as an impurity in the same reagents containing traces of sulfate, it exhibits absorption bands near 9 μ, and a clean separation of phosphate from sulfate on the alumina column was not anticipated. The results of some experiments with sulfate–phosphate mixtures are shown in Table I. First, it was found that even the smallest quantity of phosphate tested interfered with the sulfate determination if it was added to the sulfate solution *after* the chromatographic step. The interference was eliminated by the alumina column at this level. But as the quantity of phosphate was increased, the column separation broke down. The highest ratio of phosphate to sulfate which could be tolerated under the conditions of the procedure presented here was about 4 : 1 (on a weight basis as PO_4^{-3} and SO_4^{-2}). This sort of behavior was expected because previous workers had stated[8-10] that only a partial separation of phosphate and sulfate was obtainable on alumina columns. However, in most reagent chemicals, phosphate impurities are present in smaller quantities than sulfate impurities[11], so the applicability of the method is actually not badly jeopardized by phosphate.

TABLE I

EFFECT OF PHOSPHATE ON THE DETERMINATION OF 2.76 mg OF SULFATE

mg of PO_4^{-3}	*weight ratio PO_4^{-3}/SO_4^{-2}*	*mg of SO_4^{-2} found*	*error mg*	*% relative error*
1.38[a]	1 : 2	3.10	0.34	12.3
2.76[a]	1 : 1	3.42	0.66	23.9
5.52[a]	2 : 1	4.69	1.93	70.0
1.38	1 : 2	2.82	0.06	2.2
2.76	1 : 1	2.71	0.05	1.8
5.52	2 : 1	2.72	0.04	1.4
5.52	2 : 1	2.76	0.00	0.0
5.52	2 : 1	2.76	0.00	0.0
8.28	3 : 1	2.70	0.06	2.2
8.28	3 : 1	2.69	0.07	2.5
11.04	4 : 1	2.71	0.05	1.8
11.04	4 : 1	2.82	0.06	2.2
13.80	5 : 1	2.84	0.08	2.9
13.80	5 : 1	2.98	0.22	8.0
16.56	6 : 1	3.32	0.56	20.2
16.56	6 : 1	3.41	0.65	23.5
27.60	10 : 1	3.48	0.72	26.0
27.60	10 : 1	4.17	1.41	51.0

[a] In these three cases, phosphate was added *after* the chromatographic step in the procedure.

Procedure

To prepare the sample, simply dissolve a weighed quantity of the reagent-grade chemical in dilute hydrochloric acid. According to FRITZ[10], the acid concentration should not exceed about 2 *N*, but aside from this, it is not critical. The authors have used 2 to 5% by weight hydrochloric acid, which corresponds to about 0.6 to 1.6 *N*. In cases where an insoluble chloride might form, perchloric acid could be substituted for hydrochloric. The quantity of sample, and the size of the aliquot taken later for freeze-drying, can be varied, of course, depending upon the percentage of sulfate in the sample, the solubility of the sample, and other factors. In most cases, the authors dissolved a 50-g sample in 100 ml of hydrochloric acid, because it seemed preferable to use a small aliquot of a large sample in order to minimize sampling errors due to possible inhomogeneity.

Prepare an alumina column according to the directions of NYDAHL[9]. Pretreat the column and test for elutable sulfate as described[9]. Prepare the column to receive the sample by a final washing with about 10 ml of 2 to 5% hydrochloric acid. Then pass the sample through the column. A fairly rapid flow rate of 10 to 15 ml per minute is satisfactory for the column operation. Wash the column with about 50 ml of 2 to 5% hydrochloric acid solution, and then with about 30 ml of water. Now elute the sulfate by passing about 5 ml of 1 *M* ammonia followed by about 40 ml of 0.1 *M* ammonia through the column. Dilute the eluate to 50 ml in a volumetric flask.

Pipet a 1-ml aliquot of the column eluate into the bottom of a freeze-drying tube which already contains 300 mg of potassium bromide. Swirl the tube gently to dissolve the potassium bromide. Then dip the tube into a dry ice–acetone mixture with a swirling motion so that the liquid freezes in a thin layer extending partway up the wall of the tube. With the VirTis freeze-dryer, samples can be placed in the evacuated system without breaking the vacuum; in some freeze-dryers, all the samples are introduced at the same time and the system is then evacuated. In any case, keep the sample in the freezing mixture until it is to be evacuated, and then freeze-dry it overnight. Once the freeze-drying begins, the sample remains frozen without further external cooling and the process requires no attention.

Scrape the light, voluminous powder from the sides of the freeze-drying tube with a spatula, and transfer it to the die. Form the powder into an even layer, and press the disk. Various directions have been recommended for the pressing operation. The authors evacuated the die for about a minute and then pressed with a total applied force of about 20,000 lb. for 8 to 10 minutes. This force corresponds to a pressure of slightly over 100,000 lb. per sq. in. on a plunger 0.5 in. in diameter. (Several writers have apparently confused force and pressure in describing their own conditions.) Remove the disk from the die. It should be clear and unblemished, but actually slight cloudiness and surface irregularities do not seriously affect the measurement of the sulfate band at 9 μ.

Record the spectrum of the disk from about 7 to 11 μ, using a disk of 300 mg of pure potassium bromide in the reference beam. Draw the base-line on the chart, measure I and I_0, compute the transmittance, and convert this into the absorbance. Weigh the disk, and correct the absorbance value to a 300 mg basis by multiplying it by the factor (300/actual weight of disk). Compare this corrected absorbance value with a calibration curve obtained with standard sulfate samples run through the same procedure to obtain the quantity of sulfate in the freeze-dried aliquot, and then, using the appropriate dilution factors, calculate the quantity of sulfate in the original sample.

RESULTS

Pure sulfate solutions: Twenty replicate solutions of potassium sulfate were run through the entire procedure. The concentrations were such that 55.0 μg of sulfate should have been found in the disks prepared from the freeze-dried aliquots of column eluates. The actual results ranged from 53.8 to 57.0 μg, with an average value of 55.0 μg, an average deviation of 0.85 μg or 1.5%, and a standard deviation of 1.0 μg or 1.9%.

Reagent-grade chemicals: The percentages of sulfate (as SO_4^{-2}) in several reagent-grade chemicals obtained through ordinary commercial channels were determined using the procedure described above. Results are shown in Table II. Since the reliability of the analyses shown on the reagent labels was not known, it was decided to compare infrared sulfate determinations with determinations made by another method on the same samples in the same laboratory. For this comparison, the barium chloranilate colori-

TABLE II

SULFATE DETERMINATION IN SOME REAGENT-GRADE SALTS

Reagent	*Sulfate stated on label, %*	*Sulfate found, %*
KBr	0.0037	0.0034
		0.0034
		0.0032
		0.0032
$CaCl_2 \cdot 2H_2O$	0.003	0.0062
		0.0062
		0.0063
		0.0062
$NaNO_2$	0.004	0.0015
		0.0014
		0.0013
		0.0014
$Th(NO_3)_4 \cdot 4H_2O$	0.001	0.0011
		0.0011
		0.0010
		0.0011
K_2CO_3	0.002	0.0020
		0.0016
		0.0020
		0.0018
$KMnO_4$	0.005	0.0043
		0.0048
		0.0041
		0.0057
$CuCl_2 \cdot 2H_2O$	0.003	0.0031
		0.0029
		0.0030
		0.0029
$Na_2MoO_4 \cdot 2H_2O$	0.015	0.0140
		0.0148
		0.0139
		0.0155

metric method[12] was selected. Because the sulfate level in most reagents is too low for optimal results with this colorimetric method, the comparison was made in this way: 0.01 M solutions of the salts shown in Table III were "spiked" with additional sulfate, and aliquots of the solutions were analyzed by the two methods. The results in Table III show that the infrared method is consistent with the barium chloranilate method; the latter, although fairly new, is a recognized method for determining sulfate.

TABLE III

COMPARISON OF INFRARED AND BARIUM CHLORANILATE METHODS IN DETERMINING SULFATE ADDED TO REAGENT SOLUTIONS

Reagent	*Sulfate concentration in original solution, μg/ml*[a]	
	Infrared	*Ba-chloranilate*
KNO_3	424	422
$CaCl_2 \cdot 2H_2O$	594	594
$Na_2C_2O_4$	429	433
$NaHCO_3$	354	361
$CoCl_2 \cdot 6H_2O$	617	616

[a] Figures given are averages of 3 measurements.

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SUMMARY

A method for determining traces of sulfate in reagent-grade chemicals is presented. The sample is passed through an alumina column in acid solution to isolate the sulfate, which is then eluted with ammonia. Potassium bromide is added to an aliquot of the eluate, and the solution is freeze-dried. The resulting powder is pressed into a disk whose infrared spectrum is recorded. The method is reasonably accurate and requires a minimum of operator time per sample because a large number of samples can be processed together.

RÉSUMÉ

Une méthode est proposée pour le dosage de traces de sulfate dans divers produits chimiques ,,pro analysi". Le sulfate est séparé par chromatographie et dosé finalement par spectrophotométrie infrarouge.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren von Sulfat in ,,pro analysi" Chemikalien. Das Sulfat wird chromatographisch abgetrennt und infrarot-spektrophotometrisch bestimmt.

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COULOMETRISCHE PERMANGANATOMETRISCHE BESTIMMUNG DER FERROCYANID- UND JODIDIONEN

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Durch bisherige analytische Anwendung der elektrolytisch quantitativ gebildeten Permanganationen[1], wurden coulometrische Methoden zur quantitativen Bestimmung des Oxalat-, Ferro- und Arsenitions[2], sowie des Wasserstoffperoxyds[3], mit konstanter Stromstärke, ausgearbeitet.

Auf Grund der Reaktionen des Ferrocyanid- und Jodidions mit Permanganationen konnten wir die coulometrische Permanganatometrie mit konstanter Stromstärke auch auf Ferrocyanid- und Jodidionen ausbreiten und Methoden für ihre quantitative Mikro- und Halbmikrobestimmung ausarbeiten.

Bei bisher ausgearbeiteten Methoden erfolgt die Endpunktbestimmung der coulometrischen Titration durch Redox-Indikatoren[1,2], sowie potentiometrisch[4]. Bei der coulometrischen permanganatometrischen Bestimmung der Ferrocyanid- und Jodidionen ist die potentiometrische Methode die geeignetere.

Es wurde die klassische diskontinuierliche Methode, sowie diejenige mit polarisierten Indikatorelektroden aus Platin angewandt. Dabei befindet sich die Indikatorelektrode ausserhalb des Kräftefeldes, welches zwischen den Generatorelektroden herrscht[5]. Ausser Gebrauch werden Indikator- und Generatorelektroden in der Anolytenlösung aufbewahrt. Vor Ausführung der Bestimmung soll an den zu gebrauchenden Elektroden einige Minuten die Elektrolyse im System in dem die Bestimmung ausgeführt wird, durchgeführt werden[5,6].

Vor Zugabe der zu bestimmenden Substanz wird der Anolyt, durch elektrolytische Erzeugung der Permanganationen, auf das Potential des Endpunktes der coulometrischen Titration eingestellt[7,8]. In bestimmten Fällen kann die Titration auch ohne vorherige Einstellung des Anolyten ausgeführt werden, was aber nicht genügend zuverlässig ist, wobei der Erfolg sehr stark von der Reinheit und Herkunft der Indikatorelektrode aus Platin[9], sowie von der Reinheit der angewandten Chemikalien abhängt.

Unter unseren Arbeitsbedingungen, bei Anwendung der klassischen diskontinuierlichen potentiometrischen Methode, sowie der polarisierten Indikatorelektrode, betragen, in der Nähe des Endpunktes, die Zeitinkremente für elektrolytische Erzeugung der Permanganationen durch Stromstärken von 5 und 10 mA etwa 6 Sekunden. In den Systemen, mit denen wir gearbeitet haben, tritt in der Nähe des Endpunktes eine Potentialverschiebung der Indikatorelektrode nach positiveren Werten ein, besonders bei Bestimmungen von Jodidionen, und weniger bei Arbeiten mit

Ferrocyanidionen[10-12]. In der Nähe des Endpunktes sind zwei bis drei Minuten für die Potentialeinstellung nötig.

Während der Bestimmungen mit polarisierter Indikatorelektrode[8,13] wurden die Ablesungen am Mikroampèremeter 30 Sekunden nach Stromunterbrechung im coulometrischen Stromkreis vorgenommen. Das mechanische Rühren des Anolyten wurde dabei nicht unterbrochen. Als Referenzelektrode, Indikatorkathode, diente eine gesättigte Kalomelelektrode und bei einer Spannung am Potentiometer von 2 V bei 10 Ω, betrug der Widerstand, in Serie geschaltet mit der Indikatoranode, 150,000 bis 190,000 Ω.

Der Endpunkt wurde aus $E = f(t)$, $\frac{\Delta E}{\Delta t}$ und $\frac{\Delta^2 E}{\Delta t^2}$ rechnerisch nach der Methode von HOSTETTER – ROBERTS[14,15], oder graphisch festgestellt. Im System mit polarisierter Indikatorelektrode wurde der Endpunkt der Titration graphisch als Schnittpunkt der Funktion $i = f(t)$ und der Geraden $i = 0$ im Koordinatensystem $i—t$ bestimmt.

Wie auch bei anderen coulometrischen permanganatometrischen Bestimmungen[2-4] werden auch diese Bestimmungen im getrennten Anolyten unter mässigem Rühren ausgeführt.

BESTIMMUNG DER FERROCYANIDIONEN

Die Reaktionsbedingungen

$$5\,[\mathrm{Fe(CN)_6}]^{-4} + \mathrm{MnO_4}^- + 8\,\mathrm{H}^+ \rightleftarrows \mathrm{Mn}^{+2} + 5\,[\mathrm{Fe(CN)_6}]^{-3} + 4\mathrm{H_2O}$$

und die Bedingungen der elektrolytischen Erzeugung der Permanganationen ermöglichen die Ausführung dieser Titration mit elektrolytisch erzeugten Permanganationen, mit genügender Genauigkeit.

Wegen der teilweisen, unmittelbaren Oxydation des Ferrocyanids an der Anode, überzieht sich diese im Laufe der coulometrischen Titration mit einer dunklen Schicht von Ferricyanid. Beim Arbeiten im Anolyten mit 4 bis 6 *N* Schwefelsäure ist dieser Überzug an der Anode beträchtlich und die erzielten Resultate weisen einen unzulässig grossen positiven Fehler auf. In 6 *N* Schwefelsäure, bei kleineren Stromdichten und in 8 *N* Schwefelsäure, bei grösseren Stromdichten, ist die Anodenschicht bedeutend geringer und die Resultate sind befriedigend. Nach jeder Bestimmung wird die Anode in konz. Chlorwasserstoffsäure gewaschen.

Ausgeführt wurden Bestimmungen von 4 bis 33 mg Ferrocyanid, mit Stromstärken von 5.00 bis 10.08 mA, Stromdichten von 1.3 bzw. 2.5 mA/cm², bei 25 bis 30°, in 50 ml des Anolyten folgender Zusammensetzung:

(a) bei Stromdichte von 1.3 mA/cm²: 8 *N* $\mathrm{H_2SO_4}$ und 0.54 *M* oder 0.27 *M* $\mathrm{MnSO_4 \cdot 4H_2O}$, sowie 6 *N* $\mathrm{H_2SO_4}$ und 0.27 *M* $\mathrm{MnSO_4 \cdot 4H_2O}$;

(b) bei Stromdichte von 2.5 mA/cm²: 8 *N* $\mathrm{H_2SO_4}$ und 0.54 *M* oder 0.27 *M* $\mathrm{MnSO_4 \cdot 4H_2O}$.

Die Anode ist aus Platinblech von 4 cm² Oberfläche.

Das Potential der Indikatorelektrode aus Platin (P = 4 cm²) im Anolyten der angegeben Zusammensetzung hat den Wert $e_h = 0.75$ V (± 0.03). Durch elektrolytische Erzeugung der Permanganationen im Grundelektrolyten, unter den angeführten Bedingungen, bekommt das Potential der Indikatorelektrode einen positiveren Wert des Potentials des Endpunktes der Titration des Ferrocyanids mit Permanganationen,

$e_h = 0.89$ V. Die Zeitinkremente für die Erzeugung von Permanganationen bei dieser Einstellung betragen 0.1 bis 3 Sekunden, beim Ablesen des Potentials 30 Sekunden nach Unterbrechung des Stroms im coulometrischen Stromkreis. Nach Zugabe der zu untersuchenden Ferrocyanidlösung (1–6 ml 0.05 *N* $K_4[Fe(CN)_6] \cdot 3H_2O$, erreicht das Potential der Indikatorelektrode den negativeren Wert $e_h = 0.71$ V. Die coulometrische Titration wird dann wie eine potentiometrische Titration, durch Verfolgung des Potentials der Indikatorelektrode aus Platin in Bezug auf eine gesättigte Kalomelektrode, weitergeführt, mit dem Unterschied, dass die benötigten Permanganationen elektrolytisch erzeugt werden.

Bei dem System mit polarisierter Indikatorelektrode wird, nach der angegebenen Einstellung des Anolyten und nach Zugabe der zu titrierenden Lösung, das Potentiometer auf 0.89 V eingestellt und weitertitriert.

TABELLE I

50 ml des Anolyten		*Genommen* $[Fe(CN)_6]^{-4}$ *mg*	*Dauer sec*	*Gefunden* $[Fe(CN)_6]^{-4}$ *mg*	*Fehler*	
H_2SO_4 *N*	$MnSO_4 \cdot 4H_2O$ *M*				*mg*	*%*
$i = 5.00\ mA,\ D = 1.3\ mA/cm^2,\ t = 27°\ (\pm 2)$						
8	0.54	3.890	357.1	3.923	0.033	0.9
		6.483	590.9	6.490	0.007	0.1
		8.644	785.2	8.624	—0.020	—0.2
		10.81	984.7	10.81	0.00	0.0
		10.81	981.9	10.78	—0.03	—0.3
		11.16	1019.2	11.16	0.00	0.0
		12.97	996.4	12.92	—0.05	—0.4
		13.40	1226.9	13.48	0.08	0.6
8	0.27	3.890	355.9	4.908	0.018	0.5
		6.483	588.1	6.458	—0.025	—0.4
		10.81	990.7	10.88	0.07	0.6
		12.97	1191.1	13.08	0.11	0.8
6	0.27	3.890	357.1	3.922	0.032	0.8
		6.483	590.3	6.483	0.000	0.0
		10.81	987.3	10.84	0.03	0.3
		12.97	1186.2	13.03	0.06	0.5
$i = 10.08\ mA,\ D = 2.5\ mA/cm^2,\ t = 28°\ (\pm 1)$						
8	0.54	6.915	312.8	6.926	0.011	0.2
		8.644	390.4	8.643	—0.001	—0.01
		12.97	585.7	12.97	0.00	0.0
		17.29	781.4	17.30	0.01	0.1
		21.61	979.1	21.68	0.07	0.3
		27.66	1255.6	27.80	0.14	0.5
		32.42	1470.1	32.55	0.13	0.4
8	0.27	8.644	392.1	8.680	0.036	0.4
		12.97	591.1	13.09	0.12	0.9
		21.61	982.6	21.76	0.15	0.7
		32.42	1475.9	32.68	0.27	0.8

Die erzielten Resultate sind in der Tabelle I zusammengestellt und den Verlauf der Potentialänderung $E = f(t)$, bei einer coulometrischen Titration von 6.483 mg $[Fe(CN)_6]^{-4}$, mit der Stromstärke von 5.00 mA zeigt die Fig. 1.

Unter den angegebenen Bedingungen beträgt der Potentialsprung im Endpunkt, für 6 Sekunden 50–100 mV. Die Beziehung *i–t* bei einer coulometrischen Titration von

6.698 mg $[Fe(CN)_6]^{-4}$ mit einer Stromstärke von 5.00 mA, mit polarisierter Indikatorelektrode ist aus der Fig. 2 zu ersehen.

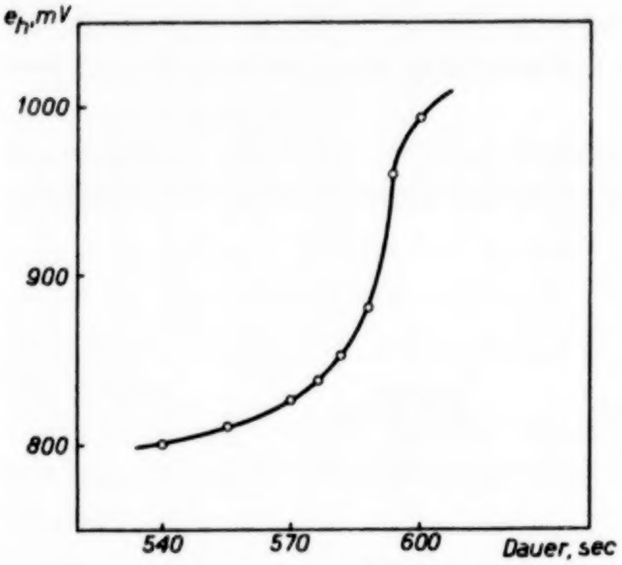

Fig. 1. $E = f(t)$. Verlauf der Potentialänderung der Indikatorelektrode aus Platin bei Titration von 6.483 mg $[Fe(CN)_6]^{-4}$ mit einer Stromstärke von 5.00 mA im Grundelektrolyten mit 8 N H_2SO_4 und 0.54 M $MnSO_4 \cdot 4\,H_2O$.

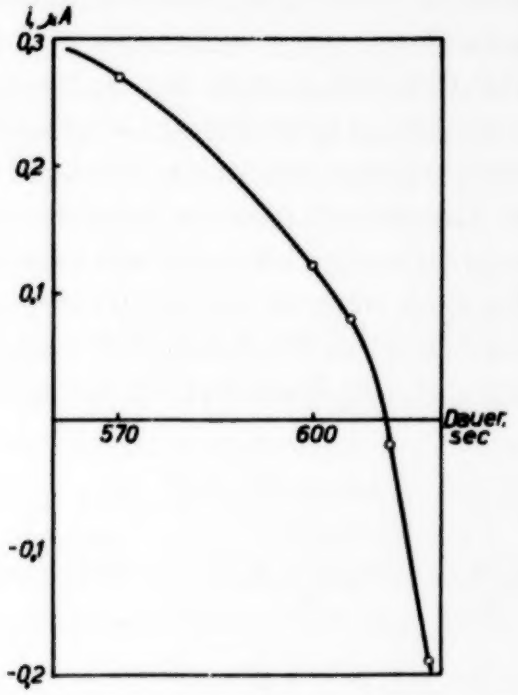

Fig. 2. Funktion i–t bei Titration von 6.698 mg $[Fe(CN)_6]^{-4}$ mit der Stromstärke von 5.00 mA an einer polarisierten Indikatorelektrode.

BESTIMMUNG DES JODIDIONS

In Anwesenheit von Schwefelsäure oxydiert Kaliumpermanganat das Jodidion bis zu elementarem Jod

$$5J^- + MnO_4^- + 8\,H^+ \rightleftarrows Mn^{+2} + 4\,H_2O + 2\tfrac{1}{2}\,J_2$$

Nach der Oxydation des gesamten Jodids oxydiert das überschüssige Permanganat das befreite Jod bis zum Jodat.

Die Bedingungen der quantitativen Reaktion der Jodid- und Permanganationen, sowie die Bedingungen der elektrolytischen Erzeugung der Permanganationen erlauben die Ausführung dieser Reaktion auch mit elektrolytisch erzeugten Permanganationen. Die Konzentration der Schwefelsäure im Anolyten, sowie die Temperatur sind auf kleinere Werte beschränkt, als bei der Bestimmung der Ferrocyanidionen, wegen der Zersetzbarkeit der Alkalijodide unter dem Einfluss stärkerer Schwefelsäure bei höherer Temperatur.

Das erzeugte elementare Jod färbt die Lösung, weswegen in diesem Falle das Reaktiv nicht als Indikator dienen kann. Direkte Anwendung eines Redox-Indikators ist ebenfalls unzulässig, sondern erst nach Überführung des Jods in eine farblose Verbindung[16,17] oder nach Extraktion des Jods während der Reaktion durch ein Lösungsmittel, wie z.B. durch Chloroform, Kohlentetrachlorid oder Benzol[18], das sich mit Wasser nicht mischt. Der Endpunkt kann ausserdem auch potentiometrisch bestimmt werden[19,20].

Wir konnten für die Endpunktbestimmung einen Indikator, sowie die potentiometrische Methode gebrauchen. Wie bei der volumetrischen Bestimmung des Jodids mit Permanganat, haben wir auch bei der coulometrischen permanganatometrischen Bestimmung die potentiometrische Methode der Endpunktbestimmung als die praktischere und zuverlässigere vorgezogen.

Es wurden 3 bis 10 mg Jodidionen, mit Stromstärken von 5.02 und 10.08 mA und Stromdichten von 0.7 bis 1.3 mA/cm² in 50 ml des Anolyten mit 4.5 N H_2SO_4 und 0.27 M $MnSO_4 \cdot 4H_2O$ bei 25° bis 30° an der Anode aus Platinspirale mit einer Oberfläche von 7.6 cm², ausgeführt.

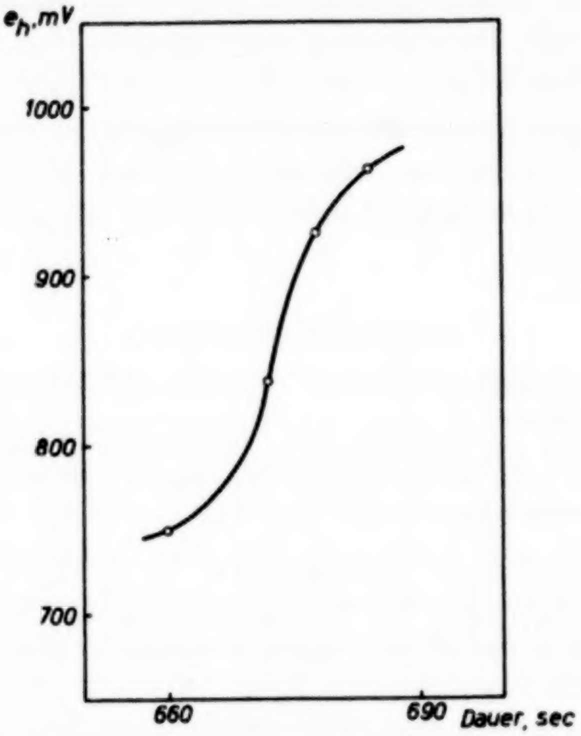

Fig. 3. $E = f(t)$. Verlauf der Potentialänderung der Indikatorelektrode aus Platin bei Titration von 4.464 mg J^- mit einer Stromstärke von 5.02 mA, ohne Anolyteinstellung.

TABELLE II

50 ml des Anolyten: 4.5 N H_2SO_4, 0.27 M $MnSO_4 \cdot 4H_2O$

Genommen J^- mg	Dauer sec	Gefunden J^- mg	Fehler	
			mg	%
$i = 5.02\ mA,\ D = 0.7\ mA/cm^2$				
3.041	458.9	3.030	—0.011	—0.4
3.144	473.7	3.128	—0.016	—0.5
3.703	563.1	3.718	0.015	0.4
4.117	624.5	4.123	0.006	0.2
4.117	623.6	4.117	0.000	0.0
4.828	729.8	4.818	—0.010	—0.2
5.517	833.7	5.505	—0.012	—0.2
6.082	922.0	6.088	0.006	0.1
6.082	914.2	6.036	—0.046	—0.8
$i = 10.08\ mA,\ D = 1.3\ mA/cm^2$				
6.222	469.9	6.223	0.001	0.02
7.857	596.9	7.914	0.057	0.8
7.857	591.7	7.842	—0.015	—0.2
8.494	635.5	8.426	—0.068	—0.8
9.335	699.7	9.277	—0.058	—0.6
10.04	759.6	10.07	0.03	0.3
10.04	755.3	10.01	—0.03	—0.3

Die erzielten Resultate enthält die Tabelle II. Die Funktion $E = f(t)$ bei der Titration von 4.464 mg Jodidionen mit einer Stromstärke von 5.02 mA zeigt die Fig. 3. Für einen Anolyten der angeführten Zusammensetzung und für die angegebenen Jodidmengen beträgt der Potentialsprung im Endpunkt, für 6 Sekunden, etwa 100–150 mV.

Das Potential der Indikatorelektrode aus Platin ($P = 4$ cm^2) im angewandten Anolyten hat den Wert $e_h = 0.73$ V. Durch elektrolytische Erzeugung der Permanganationen nimmt das Potential einen positiveren Wert, $e_h = 0.85$–0.88 V, an, wie dies schon bei der Ferrocyanidbestimmung angeführt wurde. Nach Zugabe der zu untersuchenden Lösung mit Jodidionen (1 bis 5 ml 0.05 *N* KJ) erreicht das Potential der Indikatorelektrode den Wert $e_h = 0.57$ V.

Durch diese coulometrischen permanganatometrischen Bestimmungen der Ferrocyanid- und Jodidionen wurde das Anwendungsgebiet der Grundmethode erweitert und es wurden auch weitere Möglichkeiten für die Anwendung des Coulombs als Urtitersubstanz geschaffen.

ZUSAMMENFASSUNG

Die coulometrische Permanganatometrie wurde zur quantitativen Bestimmung von Ferrocyanid- und Jodidionen angewandt.

Es wurden Mikromethoden zur coulometrischen quantitativen permanganatometrischen Bestimmung des Ferrocyanid- und Jodidiones mit konstanter Stromstärke und mit potentiometrischer Endpunktbestimmung ausgearbeitet.

SUMMARY

Micromethods have been developed for the quantitative coulometric permanganatometric determination of ferrocyanide and iodide ions at constant current strength; the end-point is determined by potentiometry.

RÉSUMÉ

Des méthodes ont été établies pour le microdosage coulométrique par permanganométrie des ions ferrocyanures et iodures, à courant constant et détermination potentiométrique du point final.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

V. AMPEROMETRIC TITRATION OF FLUORIDE WITH ALUMINUM

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INTRODUCTION

The rotated aluminum electrode (RAlE) should be a suitable indicator electrode for the direct amperometric measurement of fluoride. Experimental results in the third paper of this series[1] showed that in the proper medium the anodic depolarization current of fluoride at the RAlE is proportional to the fluoride concentration provided the latter is smaller than about $3 \cdot 10^{-4}$ *M*. Therefore, it is reasonable to expect that this electrode will be suitable for the amperometric titration of fluoride. The present paper deals with the amperometric titration of fluoride with an aluminum salt. Subsequent papers will discuss the direct amperometric titration of fluoride with thorium and zirconium, and the literature on these amperometric titrations will be discussed in these papers. Considering the great practical importance of the determination of fluoride at high dilutions we have concentrated mainly on the titration in the concentration range between 10^{-4} and 10^{-3} *M*.

Agents like aluminum and thorium ions form a series of complexes with fluoride. During the titration the composition of the mixtures of complexes formed changes with the concentration of fluoride. From the known stability constants of the various complexes it is possible to calculate the concentration of "free" fluoride (not bound to aluminum) during a titration. On this basis it is possible to calculate theoretically the amperometric titration lines. This has been done in section IV, and the calculated curves are compared with the experimental curves.

Particularly in solutions dilute in fluoride and aluminum there is no simple (stoichiometric) ratio between fluoride and aluminum at the end-point; moreover this ratio changes with the concentration of fluoride titrated. From the stability constants of the various complexes it is possible to calculate the over-all composition of the reaction product at the end-point. In Table I experimental and calculated reaction ratios are compared.

Considering the varying ratio and therefore the empirical nature of the titration in very dilute solutions in aqueous media, titrations have also been carried out in 50% ethanol in the presence and absence of varying concentrations of alkali nitrates. It has been possible to find conditions under which the composition of the reaction product was reasonably constant at the end-point. Results are given in the experimental part.

EXPERIMENTAL

Materials

Sodium fluoride solution: A stock solution was prepared which contained 2.206 g of the salt per l. This was standardized gravimetrically using the lead-chlorofluoride method[2]; the concentration was 0.0528 *M*. Dilute solutions were prepared by proper dilutions of aliquots.

Aluminum nitrate solution: A stock solution was prepared which contained 6.252 g of $Al(NO_3)_3 \cdot 9H_2O$ per l. It was standardized by the oxine gravimetric method[3] and was found to be 0.0167 *M* in Al^{+3}.

All other reagents were C. P. chemical products.

Apparatus

The electrode (RAIE) and titrating equipment have been already described[4]. For the measurement of current in the amperometric titrations a Leeds and Northrup Electrochemograph was used.

The pH of all solutions was measured with a Beckmann glass electrode pH meter. For the measurement of pH in 50% ethanol solutions the glass electrode system was used with the saturated calomel electrode in water as a reference electrode. The pH values reported have no exact significance. The glass electrode was calibrated with a phosphate buffer of known pH in water. The pH of this buffer is different in 50% ethanol. No correction for the medium effect was made since we were interested only in relative values of pH.

Amperometric titrations

Aqueous medium. Titrations of fluoride in concentrations ranging from $1 \cdot 10^{-4}$ *M* to $2 \cdot 10^{-3}$ *M* were carried out in acetate buffers of varying pH. The compositions of the buffers in the titration mixtures were: a. 0.17 *N* acetic acid + 0.02 *M* sodium acetate, pH = 3.6; b. 0.1 *N* acetic acid + 0.1 *M* sodium acetate, pH = 4.6; c. 0.1 *N* acetic acid + 0.1 *M* sodium acetate + 0.5 *M* potassium nitrate, pH = 4.5.

The values of the formation constants of the various aluminum–fluoride complexes reported by BROSSET AND ORRING[5] refer to acid solutions 0.5 *M* in potassium nitrate. In order to compare calculated with experimental titration curves, a number of experiments was carried out in the presence of 0.5 *M* potassium nitrate.

In order to test the rate of attainment of equilibrium during the titration, experiments were carried out in acetate buffers at pH 3.6 and 4.6 in which known concentrations of aluminum were added to a given fluoride mixture. After measuring the fluoride current, these mixtures were allowed to stand for varying periods of time, up to 72 h, after which the fluoride current was measured.

50% Ethanol as medium. The composition of the titration mixture was: a. 0.35 *N* acetic acid + 0.01 *M* sodium acetate, (apparent) pH = 4.0; b. 0.17 *N* acetic acid + 0.035 *M* sodium acetate, (apparent) pH = 4.8. Several experiments were done in the buffers in the presence of 0.25 to 0.5 *M* alkali nitrate (sodium, potassium or lithium nitrate).

Titration procedure

Determine the residual current in the buffer. Place 50 ml of the fluoride containing solution (adjusted to pH with buffer) into the electrolysis cell and remove oxygen by bubbling nitrogen for at least 5 min. Introduce the RAIE, start its rotation at 600 r.p.m. and connect with the SCE. Apply a potential of —0.75 V and record the fluoride current after it has attained a constant value. Start the addition of the aluminum solution from a microburet and wait until the current is constant after each increment addition of the reagent. Pass nitrogen through after each addition and over the solution during the titration. Subtract the residual current (see note) and plot the results after correcting readings for the volume increase: $(V + v)/V$ where V denotes the original volume of solution and v the volume of reagent added at any point.

Notes: (1) The residual current must be determined first in a separate experiment by recording the current in the buffer solution containing no fluoride. With our electrode it was 0.2 to 0.3 μA (anodic) in acetate buffers of pH 3.6 to 4.6, but higher values were found in unbuffered solutions of KNO_3 (0.8 μA).

(2) Immediately after the addition of aluminum the current shows a sharp decrease and then slowly decreases with time. A steady value at each point during the titration is reached in no more than 15 min, depending on the concentration of fluoride. For fluoride concentrations of the order of $1 \cdot 10^{-3}$ *M* the steady current is attained in about 5 min, but in more dilute solutions it is necessary to wait 10 to 15 min to attain a constant value.

(3) In solutions initially 10^{-3} *M* in fluoride or higher, the plot of current *versus* titrant added is not linear at the beginning of the titration, see Fig. 2, curves (1) and (2). This is mainly due to the fact that the proportionality between current and fluoride concentration at the RAlE only holds up to about $3 \cdot 10^{-4}$ *M* solutions[4]. When the initial fluoride concentration was 0.001 *M* reasonably straight lines could be plotted after addition of about 40% of the aluminum found at the end-point.

Location of end-point. In the plot of fluoride current *versus* added aluminum connect the experimental points by drawing the best fitting straight line.

False end-point (*FEP*). This corresponds to the point of intersection between the two straight lines drawn through the experimental points (see points A in Figs. 1 and 2).

True end-point (*TEP*): This corresponds to the point of intersection of the reaction line with the abscissa (point B in Figs. 1 and 2).

Note: When a reaction is complete at the end-point, the current – after correction for the residual current – should be zero. As a rule this is not the case. In general

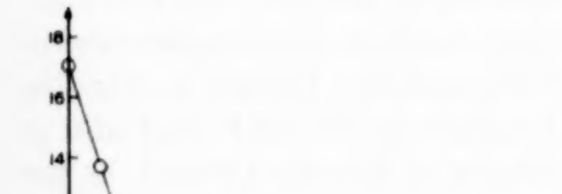

Fig. 1. Amperometric titration curves at pH 3.6. 1, $2 \cdot 10^{-4}$ *M* NaF; 2, $1 \cdot 10^{-4}$ *M* NaF. A, false end-point (FEP); B, true end-point (TEP).

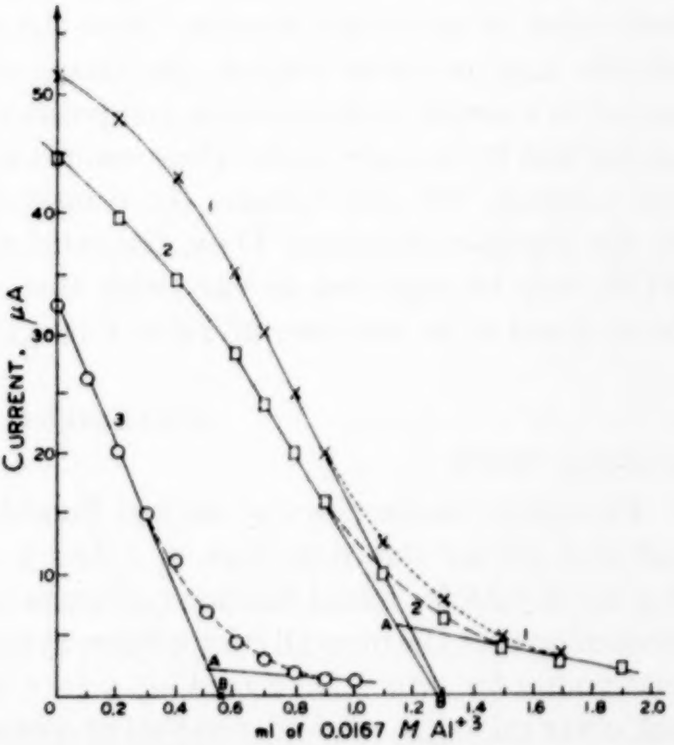

Fig. 2. Titration curves in acetate buffer of varying pH. 1, $1 \cdot 10^{-3}$ *M* NaF at pH 3.6; 2, $1 \cdot 10^{-3}$ *M* NaF at pH 4.6; 3, $5 \cdot 10^{-4}$ *M* NaF at pH 4.6. A, FEP; B, TEP.

the slopes of the reaction line and of the excess reagent line are found by using only those experimental points which are far enough removed from the end-point that according to the mass action law the reaction may be considered complete. This means that the excess reagent line should be horizontal. From Figs. 1, 2 and 3 it is seen that the excess reagent line (corrected for i_r) has quite a pronounced slope indicating that the reaction is not complete even with a large excess of reagent. Therefore, the point of intersection of the two lines (FEP) cannot correspond to a stoichiometrically defined end-point. The larger the current at the FEP the larger the concentration of unreacted fluoride. Since the reaction is not complete even with a relatively large excess of reagent, (see excess reagent lines) the TEP also cannot correspond to a simple stoichiometric composition. As a matter of fact, the "reaction line" should not be straight under these conditions, not only because of incompleteness of the reaction, but also because the composition of the complex formed is changing as the titration proceeds. Thus, the ratio of F/Al reacted at the TEP (and also at FEP) may be expected to vary with the concentration of fluoride titrated, as has been found to be the case in Table I (see DISCUSSION).

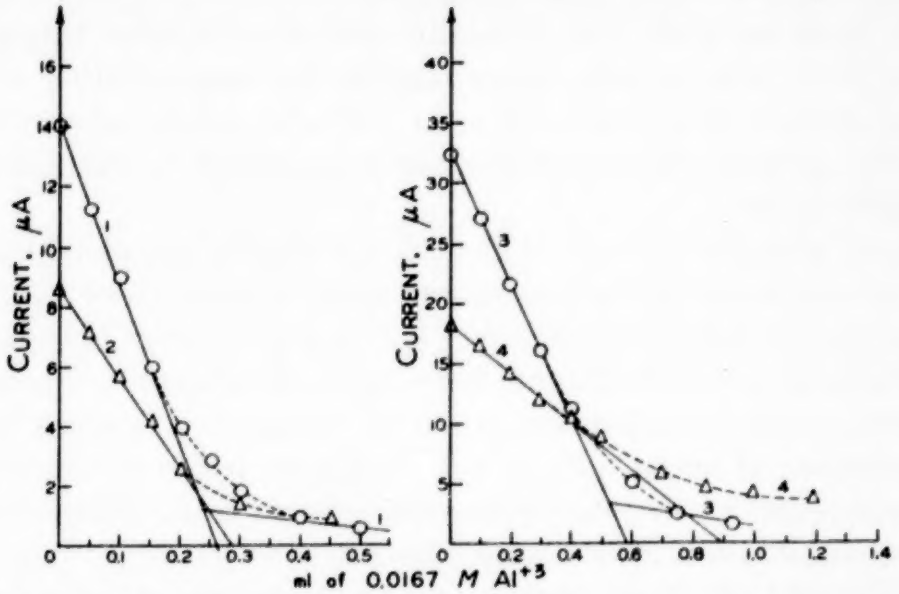

Fig. 3. Comparison of titration curves in buffered and unbuffered media of 0.5 M KNO_3. 1, $2 \cdot 10^{-4}$ M NaF in 0.1 N HAc + 0.1 M NaAc + 0.5 M KNO_3, pH 4.5; 2, $2 \cdot 10^{-4}$ M NaF in 0.5 M KNO_3, initial pH 6.5, final 5.6; 3, $5 \cdot 10^{-4}$ M NaF in 0.1 N HAc + 0.1 M NaAc + 0.5 M KNO_3, pH 4.5; $5 \cdot 10^{-4}$ M NaF in 0.5 M KNO_3, initial pH 6.5, final 5.4.

EXPERIMENTAL RESULTS

Aqueous media

Examples: Some plots at various fluoride concentrations in acetate buffers of pH 3.6 and 4.6 are shown in Figs. 1, 2 and 3. At the TEP the currents were 1.8, 2.5, 6.5 and 8.5 μA for initial fluoride concentrations of 1, 2, 5, 10 and $20 \cdot 10^{-4}$ M.
Assuming that the over-all composition at the TEP corresponds to AlF_3, the calculated end-points for $1 \cdot 10^{-4}$ M, $2 \cdot 10^{-4}$ M, $5 \cdot 10^{-4}$ M and $1 \cdot 10^{-3}$ M fluoride should be 0.106 ml, 0.212 ml, 0.529 ml, and 1.058 ml of 0.0167 M Al^{+3} as compared to the experimental values 0.152 ml, 0.275 ml, 0.54 ml and 1.28 ml respectively.

In Table I are reported the experimental fluoride/aluminum ratios at the FEP and TEP. At initial fluoride concentrations of 1 and $2 \cdot 10^{-4}$ M the values at the TEP

TABLE I

Comparison between the experimental F/Al ratio at end-point and the theoretical value.

NaF concentration M	*Fluoride–aluminum ratio*		
	FEP	*TEP*	*Calculated at TEP*[a]
a. in 0.17 *N* HAc + 0.02 *M* NaAc	pH = 3.6		
$1 \cdot 10^{-4}$	2.11	2.09	2.17
$2 \cdot 10^{-4}$	2.44	2.36	2.42
$1 \cdot 10^{-3}$	2.62	2.40	3.05 2.60[b]
$2 \cdot 10^{-3}$	2.62	2.35	3.30 2.8 [b]
b. in 0.1 *N* HAC + 0.1 *M* NaAc	pH = 4.6		
$1 \cdot 10^{-4}$	2.21	2.10	2.22
$2 \cdot 10^{-4}$	2.79	2.61	2.50
$5 \cdot 10^{-4}$	3.05	2.94	2.85
$1 \cdot 10^{-3}$	2.88	2.48	3.10 2.7 [b]
c. as b + 0 5 *M* KNO_3	pH = 4.5		
$2 \cdot 10^{-4}$	2.65	2.44	2.50
$5 \cdot 10^{-4}$	2.93	2.72	2.85
$1 \cdot 10^{-3}$	2.99	2.54	3.10 2.7 [b]

[a] Calculated values correspond to solutions of ionic strength $\mu = 0.5$.

[b] See discussion.

and FEP do not differ much (Table I). In more concentrated solutions ($1 \cdot 10^{-3}$, $2 \cdot 10^{-3}$ *M* fluoride) there is much greater uncertainty in the determination of the end-points, because of the more pronounced curvature of the titration lines, the high currents at the end-point(s) and the pronounced slope of the excess reagent lines.

Titrations were also carried out at different concentrations of fluoride in acetate

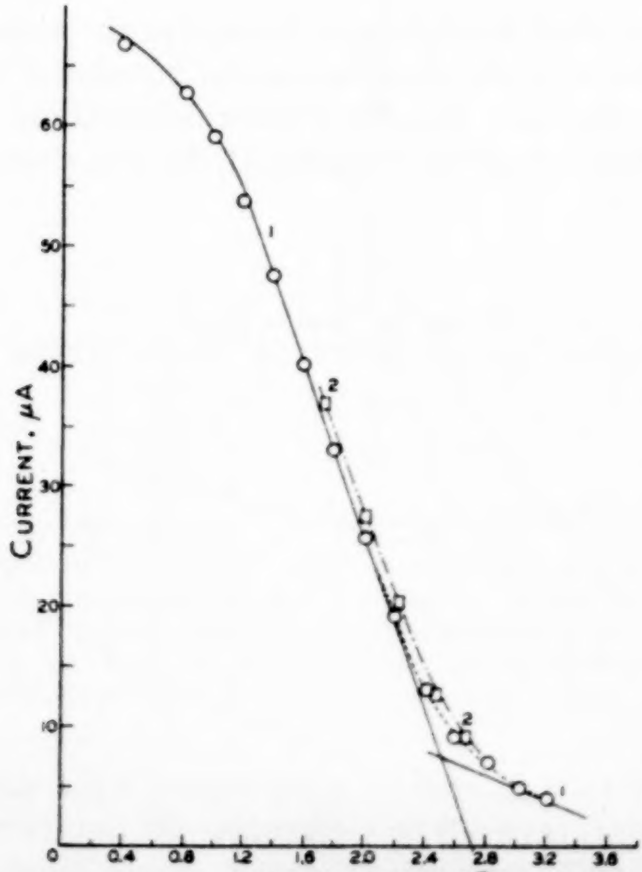

Fig. 4. Effect of time of waiting upon titration curve after addition of aluminum. 1, titration curve of $2 \cdot 10^{-3}$ *M* NaF at pH 3.6; 2, current readings after standing for 72 h.

buffers which were 0.5 *M* in potassium nitrate and also in 0.5 *M* potassium nitrate solutions containing no buffer. Examples of the titration lines are presented in Fig. 3. In the acetate buffer (pH 4.6) the presence of 0.5 *M* potassium nitrate has hardly any effect on the results (Table I). In an unbuffered 0.5 *M* potassium nitrate the results are irregular and poorly reproducible. This may be accounted for in part by the fact that the pH during the titration decreased from 6.5 to about 5.5.

Time of attainment of equilibrium during the titration

Two sets of titrations were carried out of a $2 \cdot 10^{-3}$ *M* fluoride solution both in acetate buffers of pH 3.6 and of pH 4.6. One titration was carried out according to the procedure described above. In the other "titration" mixtures were made containing 80, 90, 100, 111 and 120% respectively of aluminum, the percentage based on the formation of AlF_3. The mixtures (at pH 3.6 and 4.6) were allowed to stand for up to 72 h. The mixtures were then transferred to the electrolysis cell and the fluoride current was measured. In most of the mixtures no precipitate was observed. If a precipitate was visible, the mixture was centrifuged and the fluoride current was measured again. The fluoride concentration was calculated using a calibration curve determined in the same supporting electrolyte as in the mixtures. As is illustrated in Fig. 4 the results by the direct titration were the same (within 3%) as those obtained from titration lines constructed after a waiting period of 72 h. Titrations were also carried out at pH 2 (0.01 *N* perchloric acid). In such a medium the reaction between fluoride and aluminum was found highly incomplete, but equilibrium was established within 40 min.

Titrations in 50% ethanol

From Fig. 5 it is clear that fluoride ions depolarize the aluminum electrode in a 50% ethanol medium but that the limiting current is reduced to about one half the value found in aqueous medium. Results of fluoride titrations in an acetate buffer of pH 4.0 in 50% ethanol are given in Table II. In the absence of added sodium

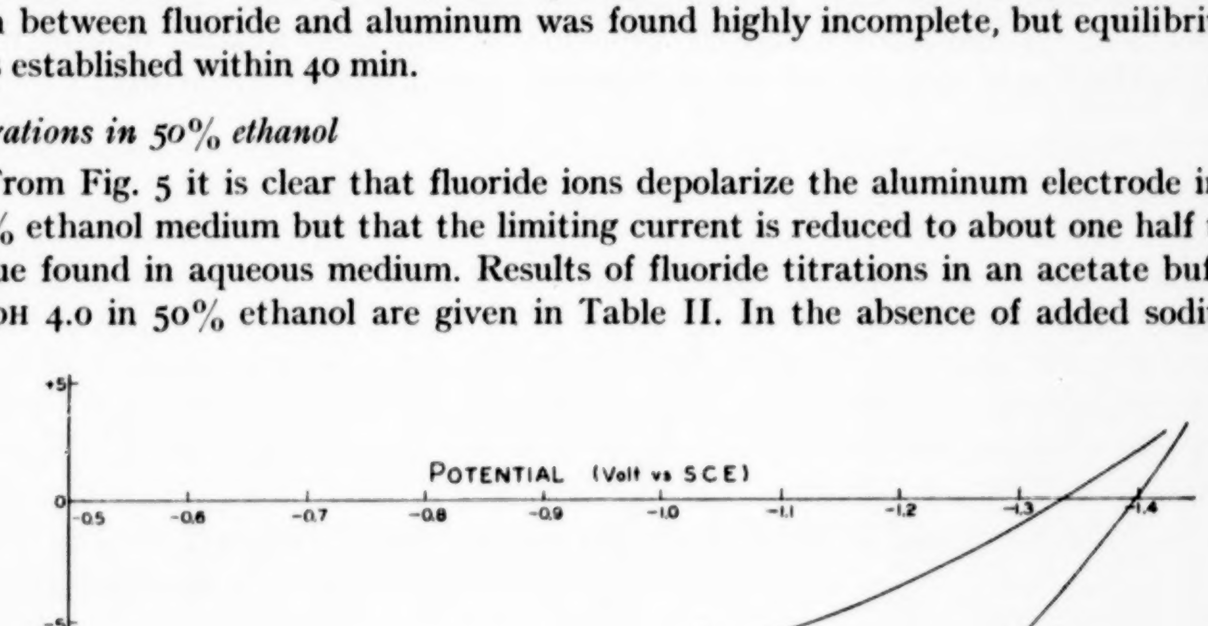

Fig. 5. Comparison of current–potential curves of fluoride in water and 50% ethanol. 1, $2 \cdot 10^{-4}$ *M* NaF in acetate buffer pH 4.0, aqueous medium; 2, same as 1, in 50% ethanol, pH 4.0.

TABLE II

Effect of sodium nitrate on fluoride/aluminum ratios at the end-point in 50% ethanol solutions buffered with 0.35 N HAc + 0.01 M NaAc, pH 4.0.

NaF concentration *M*	*$NaNO_3$ concentration* *M*	*F/Al ratio*	
		FEP	*TEP*
$2 \cdot 10^{-4}$	0	3.0	2.75
	0.2	5.0	4.1
	0.5	6.2	5.7
$5 \cdot 10^{-4}$	0	3.3	3.0
	0.2	6.0	5.8
	0.5	6.1	5.9
$1 \cdot 10^{-3}$	0	5.5	4.7
	0.2	6.1	5.8
	0.5	6.1	6.0

nitrate the F/Al ratio at the TEP increases from 2.75 with $2 \cdot 10^{-4}$ M fluoride to 4.7 with $1 \cdot 10^{-3}$ M fluoride. Addition of sodium nitrate in a concentration of 0.5 M greatly improves the situation and in the range of fluoride concentrations studied the F/Al ratio at the end-point was found to be 5.9 ± 0.1. Examples of titration lines are given in Figs. 6 and 7.

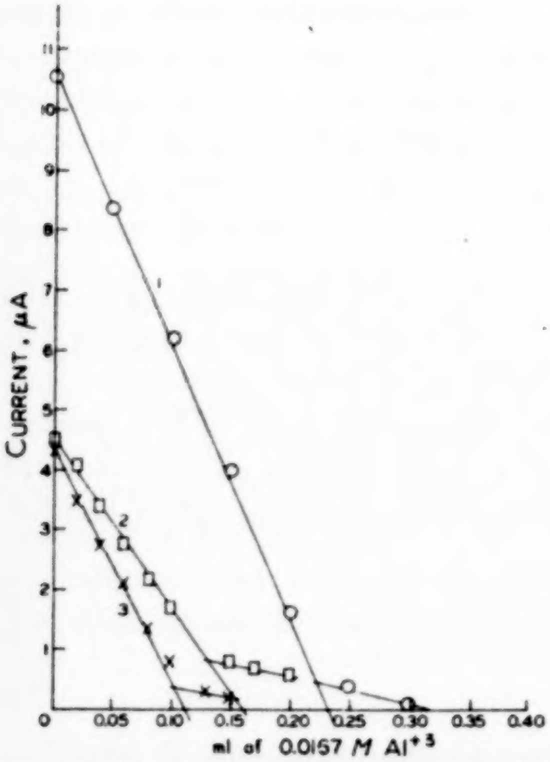

Fig. 6. Effect of $NaNO_3$ concentration on titration of $2 \cdot 10^{-4}$ M NaF in 50% ethanol, pH 4.0. 1, no $NaNO_3$; 2, 0.2 M in $NaNO_3$; 3, 0.5 M in $NaNO_3$.

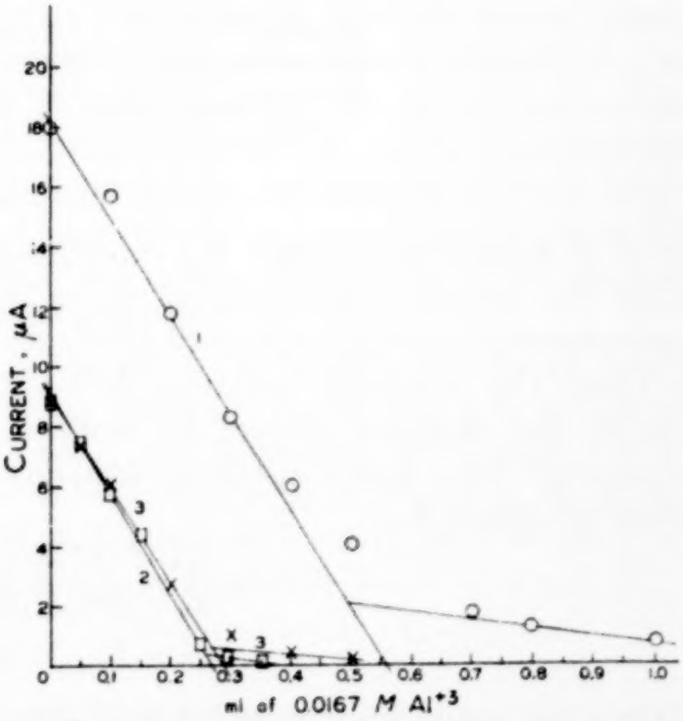

Fig. 7. Effect of $NaNO_3$ concentration on titration of $5 \cdot 10^{-4}$ M NaF in 50% ethanol, pH 4.0. 1, no $NaNO_3$; 2, 0.2 M in $NaNO_3$; 3, 0.5 M in $NaNO_3$.

From results in Table III it is interesting to note that at the same concentration (0.5 M) potassium nitrate has the same effect on the F/Al ratio at the TEP as sodium nitrate has, while lithium nitrate hardly exerts any effect. It would appear that Na_3AlF_6 and K_3AlF_6 are considerably more stable or less soluble in the salt containing buffer in 50% ethanol than Li_3AlF_6 is.

TABLE III

Effect of kind of alkali nitrate (0.5 *M*) on the F/Al ratio in 50% ethanol buffered with 0.35 *N* HAc + 0.01 *M* NaAc, pH 4.0

NaF concentration M	*Salt present*	*F/Al ratio*	
		FEP	*TEP*
$2 \cdot 10^{-4}$	$NaNO_3$	6.2	5.7
	KNO_3	6.6	5.7
$5 \cdot 10^{-4}$	$NaNO_3$	6.1	5.9
	KNO_3	5.9	5.8
	$LiNO_3$	5.5	3.5
$1 \cdot 10^{-3}$	$NaNO_3$	6.1	5.9
	KNO_3	6.1	5.9
	$LiNO_3$	4.2	3.7

Although the reproducibility of the experiments in Table III is no better than 5%, it appears possible to titrate fluoride in the buffer (pH 4.0) in 50% ethanol in the presence of 0.5 *M* sodium or potassium nitrate with an accuracy of about 10%. Three unknowns (to the operator) were titrated. Taking a reaction ratio of F/Al of 6, the following results were obtained:

	fluoride present (M)	*fluoride found (M)*
solution 1	$2.5 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
solution 2	$5.5 \cdot 10^{-4}$	$5.4 \cdot 10^{-4}$
solution 3	$8.3 \cdot 10^{-4}$	$8.9 \cdot 10^{-4}$

DISCUSSION

It is of interest to compare the experimental titration curves with those calculated from the various equilibrium constants and also to compare at the end-point the experimental reaction ratio with that calculated from equilibrium constants.

Using the customary notation[6] Al^{+3} and F^- are designated as M and L, respectively, and electrical charges are omitted. M and L form a series of mononuclear complexes ML_n, with consecutive equilibrium constants K_n and cumulative equilibrium constants β_n:

$$K_n = [ML_n]/[ML_{n-1}]\,[L] \qquad (1)$$

$$\beta_n = [ML_n]/[M]\,[L]^n \qquad (2)$$

$$\beta_n = K_1 \ldots . K_n \qquad (3)$$

When the ligand may be protonated the ordinary acid dissociation K_a is used:

$$K_a = [H^+]\,[L]/[HL] \qquad (4)$$

The total concentrations of M and L, respectively, in all forms are:

$$\begin{aligned} C_M &= [M] + [ML] + [ML_2] + \ldots . \\ &= [M]\,\{1 + \beta_1[L] + \beta_2[L]^2 + \ldots .\} \qquad (5) \end{aligned}$$

$$\begin{aligned} C_L &= [L] + [HL] + [ML] + 2[ML_2] + \ldots . \\ &= [L]\left(1 + \frac{[H^+]}{K_a}\right) + [M]\,\{\beta_1[L] + 2\beta_2[L]^2 + \ldots .\} \qquad (6) \end{aligned}$$

In the titration of L with M let the initial total concentration of L, *i.e.*, $[L] + [HL]$, be C_L, and let the number of moles of M added per total mole of L be r, *i.e.*, $C_M = r \cdot C_L$. From the equations above it follows directly that

$$r = \left(1 - \frac{[L]\,(1 + [H^+]/K_a)}{C_L}\right) \frac{1}{\bar{n}} \quad \ldots \ldots \ldots \quad (7)$$

where $\bar{n}$ is the average ligand number, *i.e.*, moles of L bound per mole of M, defined by (8):

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \ldots}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots} \quad \ldots \ldots \ldots \quad (8)$$

When a physical measurement (*e.g.*, current in an amperometric titration) is made which is directly proportional to $[L]$, and if pH and volume are constant during the titration, equation (7) becomes

$$r = \left(1 - \frac{i}{i_0}\right) \frac{1}{\bar{n}} \quad \ldots \ldots \ldots \quad (9)$$

where i_0 and i are respectively the initial current and current after the addition of r moles of M per mole of L.

Equation (9) permits the simple and exact calculation of titration curves, given the values of K_n. It is emphasized particularly that while the calculation of r in terms of i/i_0 is simple and exact, requiring no approximation, the reverse calculation of i/i_0 in terms of r in general cannot be carried out exactly. There is an entirely analogous situation (generally overlooked) in acid–base calculations. Given a polybasic acid, the calculation of pH after the addition of a given amount of base generally must be carried out approximately, whereas the reverse calculation of the amount of base required to reach a given pH is easy and exact.

The calculation of the titration curve is carried out as follows. The initial value of $[L]$ is calculated from the known C_L and pH. Using the known K_n, $\bar{n}$ is calculated from equation (8) for $[L]$ equal to 1.0, 0.8, 0.6,... etc. times the initial value, corresponding to i/i_0 equal to 1.0, 0.8, 0.6, ... Substitution in (9) gives r. As an example, the calculated titration curves of $2 \cdot 10^{-4}$ *M* and $2 \cdot 10^{-3}$ *M* F^- with Al^{+3}, at pH such that $[HF]$ is small compared to $[F^-]$, are given in Table IV.

TABLE IV

Calculated titration curves of F^- with Al^{+3}; $[HF] \ll [F^-]$; $\mu = 0.53$

i/i_0	$C_F = 2 \cdot 10^{-4}\,M$		$C_F = 2 \cdot 10^{-3}\,M$	
	$\bar{n}$	r	$\bar{n}$	r
1.0	2.63	0	3.52	0
0.8	2.54	0.079	3.44	0.058
0.6	2.43	0.165	3.33	0.120
0.4	2.28	0.263	3.18	0.189
0.2	2.02	0.396	2.90	0.276
0.1	1.77	0.508	2.63	0.342
0.01	0.90	1.10	1.77	0.560

The following equilibrium constants are those reported by BROSSET AND ORRING[5]: $\log K_1 = 6.13$, $\log K_2 = 5.02$, $\log K_3 = 3.85$, $\log K_4 = 2.74$, $\log K_5 = 1.63$, $\log K_6 = 0.47$, which apply at 25° and an ionic strength of 0.53. A series of such calculated titration curves for C_F from $2 \cdot 10^{-5}$ *M* to $5 \cdot 10^{-3}$ *M* is shown in Fig. 8.

In practice it is advisable to calculate exact values of $\bar{n}$ covering the range of [L] of interest and plot $\bar{n}$ *vs.* –log [L]. (This also facilitates calculation when the concentration of HL must be considered, *vide infra*). Values of $\bar{n}$ for the Al^{+3}–F^- system are given in Table V. Many of these values have been given previously by BROSSET.

TABLE V

Average ligand number at various $[F^-]$ (25°, $\mu = 0.53$)

$-\log [F^-]$	$\bar{n}$	$-\log [F^-]$	$\bar{n}$
8	0.013	2.5	3.72
7	0.121	2	4.16
6	0.66	1.5	4.61
5.5	1.07	1.0	5.04
5	1.51	0.5	5.43
4.5	1.94	0.0	5.73
4	2.38	—0.5	5.90
3.5	2.82	—1.0	5.98
3	3.26		

Calculation of end-points

If the decrease in current (or other quantity directly proportional to concentration) upon addition of reagent is linear before the equivalence point, the latter is found by extrapolation of the straight line to zero current. Equation (9) shows that a linear decrease occurs only if $\bar{n}$ is constant over the range of [L] covered by the titration. This situation does not exist in the system Al^{+3}–F^- in aqueous medium. Actually

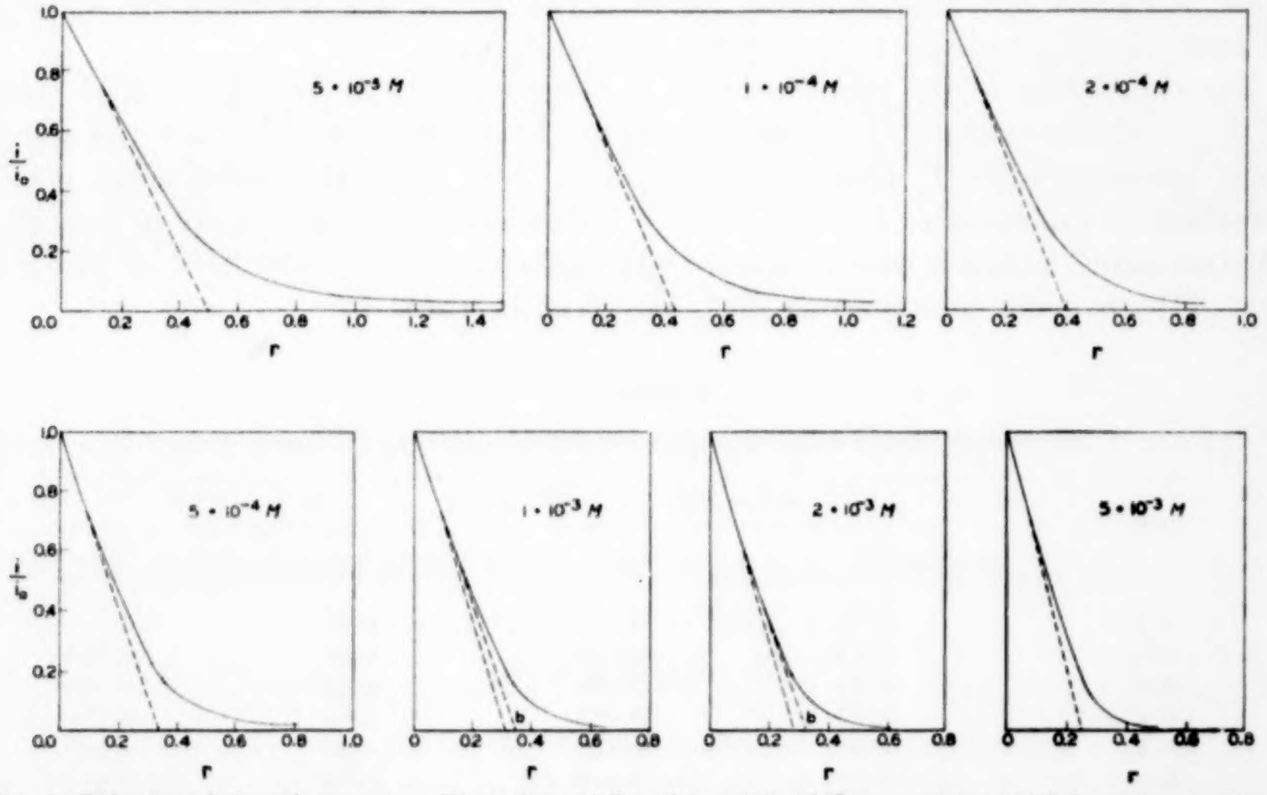

Fig. 8. Calculated titration curves. Titration of fluoride with Al^{+3} at various initial concentrations of F^-. $\mu = 0.53$, 25°; $[HF] \ll [F^-]$; r = moles Al^{+3} added per mole F^-.

over the range $[\mathrm{F}^-]$ from 10^{-6} *M* to 10^{-1} *M*, $\bar{n}$ varies practically linearly with log $[\mathrm{F}^-]$, from 0.66 to 5.04. (Table V). Therefore all the titration lines must be curved (Fig. 8), in agreement with the experimental results (Figs. 1–3).

The extrapolation of curves (Fig. 8) to the end-point is not objective but involves personal judgment. If the curve approximates a straight line for the first half of the titration, it appears reasonable to assume that the straight line drawn through the points would have a slope about equal to the average of the slopes at 0% and 50% of the titration. Equation (9) shows that the mole ratio of L to M at the extrapolated end-point (TEP) would be $\frac{1}{2}(\bar{n}_0 + \bar{n}_{\frac{1}{2}})$, where $\bar{n}_0$ and $\bar{n}_{\frac{1}{2}}$ are the average ligand numbers corresponding to the initial *free* fluoride concentration and to half the initial concentration, respectively. Values derived in this way are given in Table VI. A plot of $\bar{n}_{\mathrm{TEP}}$ *versus* log of initial fluoride concentration yields a straight line.

TABLE VI

Calculated mole ratios at TEP, titration of F^- with Al ($\mu = 0.53$; 25°)

Initial F^- *M*	$\bar{n}_{\mathrm{TEP}}$
$5 \cdot 10^{-5}$	1.98
$1 \cdot 10^{-4}$	2.25
$2 \cdot 10^{-4}$	2.51
$5 \cdot 10^{-4}$	2.86
$1 \cdot 10^{-3}$	3.13
$2 \cdot 10^{-3}$	3.39
$5 \cdot 10^{-3}$	3.75

Finally, if the pH is such that $[\mathrm{HF}]$ is not negligible compared to $[\mathrm{F}^-]$, the necessary correction is simple. For example, in the titration of $4 \cdot 10^{-3}$ *M* fluoride at pH $= \mathrm{p}K_a = 2.94$, one half of the fluoride not bound to aluminum is present as HF. Therefore this titration should be identical with that of $2 \cdot 10^{-3}$ *M* fluoride at pH $> \mathrm{p}K_a$. In general, the ratio $[\mathrm{F}^-]/C_{\mathrm{F}}$ is calculated from the evident relation

$$\frac{[\mathrm{F}^-]}{C_{\mathrm{F}}} = \frac{K_a}{K_a + [\mathrm{H}^+]}$$

and the value of $\bar{n}_{\mathrm{TEP}}$ read from a plot of Table VI.

In this way the calculated values of n_{TEP} given in Table I have been derived. It will be noted that the calculated mole ratios in the titration of $1\text{–}5 \cdot 10^{-4}$ *M* fluoride are in remarkably good agreement with the experimental ratios found at the TEP. The deviation becomes greater at fluoride concentrations of $1\text{–}2 \cdot 10^{-3}$ *M*. It has been mentioned – and it is illustrated again in Fig. 2 – that at these high fluoride concentrations the current is not linearly proportional to fluoride concentration. In the titration of $1 \cdot 10^{-3}$ *M* fluoride (curves 1 and 2, Fig. 2) the current *vs.* reagent curve became approximately linear after about 30% of the free fluoride had disappeared and remained virtually straight until about 65% had reacted. Using this portion of the calculated curve (Fig. 8) the extrapolated F/Al ratios at the TEP are approximately 2.7 (pH 4.6) and 2.6 (pH 3.6) which, as was to be expected, are in much better agreement with the experimental values (2.48 and 2.40, respectively) than the values obtained by extrapolation of the initial slope of the line. In a similar way the values have been found for the titration of $2 \cdot 10^{-3}$ *M* fluoride. These have been added to Table I with the designation (b).

As a further test of agreement between the experimental and calculated titration curves the experimental values of i/i_0 at the true end-point were compared with the theoretical values read from Fig. 8. In $1 \cdot 10^{-3}$ *M* fluoride solution the (initial) current i_0 is less than proportional with fluoride concentration. Therefore, in the calculation of i/i_0 from curve 2 in Fig. 2 in the titration of $1 \cdot 10^{-3}$ *M* fluoride, i_0 was taken equal to twice the value of i_0 in the titration of $5 \cdot 10^{-4}$ *M* fluoride (curve 3, Fig. 2). Also, in the titration of $1 \cdot 10^{-3}$ *M* fluoride the calculated end-point was taken equal to that given in the last column of Table I (with designation (b)). It is evident from Table VII that the experimental and calculated values of i/i_0 at the TEP are in excellent agreement.

TABLE VII

Comparison of theoretical and experimental values of i/i_0 at the TEP

Initial fluoride concentration *M*	i/i_0 *found*	i/i_0 *calculated*
$1 \cdot 10^{-4}$	0.20	0.20
$2 \cdot 10^{-4}$	0.18	0.19
$5 \cdot 10^{-4}$	0.17	0.18
$1 \cdot 10^{-3}$	0.10	0.10
$2 \cdot 10^{-3}$	0.07	0.09

The agreement between calculated and experimental titration curves is very gratifying. However, from the practical point of view the amperometric titration of fluoride with aluminum in aqueous acetate buffers is not attractive because the ratio of fluoride to aluminum reacted at the end-point increases with increasing initial concentrations of fluoride (Table I). Thus a calibration curve determined under the same experimental conditions must be constructed. Addition of much potassium nitrate hardly affects the results.

When the titration is carried out in an acetate buffer (pH 4.0) in a medium of 50% ethanol, the reaction ratio at the true end-point is greater than in water, but again increases considerably with increasing initial fluoride concentration (Table II). When the buffered medium of 50% ethanol is made 0.5 *M* in potassium or sodium nitrate, a constant reaction ratio of 5.9 ± 0.1 is found at the true end-point in a concentration range of fluoride between $2 \cdot 10^{-4}$ *M* and $2 \cdot 10^{-3}$ *M*. Thus no calibration curve is necessary and this reaction medium can be recommended for the amperometric titration of fluoride.

The average value of the reaction ratio is 5.9, slightly less than is necessary for the formation of Na_3AlF_6 or K_3AlF_6. In this connection it is of interest to mention that BROSSET AND WAHLBERG[7] in the precipitation of potassium aluminum fluoride from aqueous solutions, which were 0.5 *M* in potassium nitrate, found a composition corresponding to $K_3AlF_{5.9}$. When sodium instead of potassium nitrate was used, the composition corresponded to about $Na_3AlF_{5.6}$. The X-ray pattern of these precipitates closely resembled that of cryolite.

ACKNOWLEDGEMENT

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SUMMARY

The rotated aluminum electrode is a suitable indicator electrode in the amperometric titration of fluoride. Fluoride in concentrations varying between $1 \cdot 10^{-4}$ and $2 \cdot 10^{-3}$ *M* was titrated with

a standard aluminum nitrate solution in aqueous buffer solutions (pH between 3.6 and 4.6). Equilibrium was established within 15 min. The fluoride–aluminum ratio at the (true) end-point was found to increase from 2.2 in 10^{-4} *M* fluoride to 2.8 in $2 \cdot 10^{-3}$ *M* fluoride. The titration calculated from the stability constants of the various aluminum–fluoride complexes were found to be in excellent agreement with the experimental curves.

From a practical point of view titration in an acetate buffer in 50% alcohol in the presence of 0.5 *M* potassium or sodium nitrate is recommended. The fluoride–aluminum ratio at the end-point was found to be 5.9 ± 0.1 and independent of the fluoride concentration.

RÉSUMÉ

L'électrode rotative d'aluminium peut être utilisée pour le titrage ampérométrique des fluorures, au moyen d'une solution étalon de nitrate d'aluminium. Les courbes de titrage, calculées à partir des constantes de stabilité des divers complexes aluminium–fluorure, correspondent très bien aux courbes expérimentales.

ZUSAMMENFASSUNG

Es wird die Eignung der rotierenden Aluminiumelektrode zur amperometrischen Bestimmung von Fluorid mit einer Aluminiumnitratlösung beschrieben. Die auf der Basis der Stabilitätskonstanten der verschiedenen Aluminium–Fluorid Komplexen berechneten Titrationskurven stimmen sehr gut mit den experimentell erhaltenen Kurven überein.

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THE DETERMINATION OF CARBOXYL GROUPS IN POLYETHYLENE TEREPHTHALATE

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INTRODUCTION

The carboxyl content of polyethylene terephthalate can be used for the characterisation of this polymer. This content may be considered as a measure of the thermal degradation[1,2], and from it and from the hydroxyl content the average molecular weight of the polymer can be calculated[3].

WARD[4] describes an IR-spectrophotometric method. POHL[5] discusses a volumetric method applied by CONIX[3] in work on the determination of the average molecular weight of polyethylene terephthalate. POHL's method has the advantage over that of WARD[4] that it does not need an IR-spectrophotometer. The method involves dissolution of a 100–200-mg sample in benzyl alcohol at 203°, mixing the solution with chloroform whereby a metastable solution is formed, and titration with benzyl-alcoholic sodium hydroxide solution to phenol red indicator. The value thus found must be corrected for the amount of carboxyl groups that are formed during the dissolution at this high temperature. This correction is proportional to the time necessary for complete dissolution and is independent of the initial carboxyl content of the sample.

POHL[5] prefers dissolution in hot benzyl alcohol to that in acidic, phenolic solvents, in which the sample can be dissolved at much lower temperatures, because in the latter case the end-point indication is obscured.

Although the method yields precise results and requires less time for a determination, it still has some disadvantages. First, it is always necessary to apply the correction mentioned. Second, the solvent used, *viz.* benzyl alcohol, must be of high purity and free from water, lest hydrolysis at the high temperature during dissolution should take place. It was therefore decided to study the possibility of a determination in another solvent that would not involve the disadvantages mentioned.

EXPERIMENTAL

Two requirements must be met by the solvent used, *viz.* the sample should dissolve at such a temperature that no thermal degradation occurs, and its acidity should be much lower than that of the carboxyl group to be titrated.

Preliminary tests showed that 2 g of the polymer dissolve in 50 ml of a mixture of *o*-cresol and chloroform (70 + 30 g) by heating on a hot plate for 20 min. In this way solution could be effected at about 90°. As the results of the determinations were found to be independent of the dissolution time, it may be concluded that no thermal degradation occurs. After cooling to room temperature the solution remained clear. These solvents were purified in order to reduce the blank value as far as possible. The solution thus obtained was titrated potentiometrically with 0.1 *N* ethanolic potassium hydroxide solution.

The difference in potential at the equivalence point was about 100 mV. In this titration a model H 2 Beckman pH-meter and an S.C.E. and a glass electrode were used. Precise results could be obtained in this way.

In order to check the method, the determination of the carboxyl groups of polyethylene terephthalate in the above-mentioned mixture of *o*-cresol and chloroform by H.F. titration with 0.05 *N* ethanolic sodium hydroxide solution was also examined. It proved necessary to increase the conductivity of the solution by the addition of 10 ml of acetone; the solution again remained clear. The H.F. apparatus used was constructed in collaboration with the physical department of the N.V. Research. During the titration the frequency was kept constant at 0.6 MHz and the grid current was plotted against the amount of titrant added. From the resulting graph the equivalence point was determined. During the titration the solution was stirred mechanically. The stirrer was only stopped when the grid current was read.

The results obtained by these two methods were compared with those obtained according to POHL's method. This method was slightly modified in this company's Polyester Department; chloroform was added to the benzyl alcoholic solution instead of the reverse, so that the titration could be carried out in the vessel used for dissolution. The correction factor was found to be 2.4 mequivs. per kg per min. It was determined on several samples and found to be independent of the initial carboxyl content of the sample, which agrees with POHL's statement.

Seven samples of polyethylene terephthalate were analysed in triplicate by the three methods mentioned, *viz.* visually according to POHL, potentiometrically, and by H.F. titration. The samples used were ground in a Wiley mill. The potentiometric procedure, which is recommended, is given in detail at the end of this paper. The equivalence points in these potentiometric titrations were calculated by interpolation according to HAHN[6]. The results obtained are listed in Table I, which also gives the differences between the mean results of the three methods for each sample, d_i, the mean values of these differences, $\bar{d}_i$, and the standard deviations of single determinations by the respective methods.

The potentiometric method required 2-g samples and the visual method 0.2-g samples, hence it was investigated whether the sample size in the first method could be decreased, so that a better comparison between the two methods would be obtained.

When 200-mg portions of samples 3 and 7 (Table I) were dissolved in the *o*-cresol–chloroform mixture and titrated with 0.02 *N* ethanolic potassium hydroxide solution, the results were somewhat high, compared with the *y*-values of Table I. Better results

TABLE I

CARBOXYL CONTENT OF POLYETHYLENE TEREPHTHALATE IN MEQUIVS. PER KG

Sample	*Visually in benzyl alcohol and chloroform* x	*Potentiometrically in o-cresol and chloroform* y	*HF-titration in o-cresol, chloroform and acetone* z	$d_1 = \bar{x} - \bar{y}$	$d_2 = \bar{x} - \bar{z}$	$d_3 = \bar{y} - \bar{z}$
1	22.5	22.3	23.7			
	22.4	21.9	21.3	—0.1	—0.1	0
	22.1	23.0	22.2			
2	21.9	22.8	20.9			
	23.0	22.4	21.6	—0.5	+1.0	+1.5
	21.0	22.2	20.5			
3	79.8	81.0	81.1			
	80.3	80.6	80.2	—0.1	—0.6	—0.5
	80.8	79.7	81.3			
4	25.8	25.1	25.0			
	22.5	24.0	23.7	—0.8	—0.2	+0.6
	24.2	25.9	24.5			
5	32.9	31.0	30.6			
	29.5	30.4	31.1	+0.2	+0.6	+0.4
	31.5	31.0	29.6			
6	23.2	23.3	23.2			
	25.1	22.5	22.6	+1.7	+1.2	—0.5
	25.6	23.0	24.3			
7	58.3	60.0	59.2			
	59.6	59.8	57.3	—0.7	+0.9	+1.6
	58.8	58.9	57.5			
mean $\bar{d}_i$				0	+0.4	+0.4
st. dev.	$s_x = 1.05$	$s_y = 0.58$	$s_z = 0.86$	$s_{d_1} = 0.85$	$s_{d_2} = 0.70$	$s_{d_3} = 0.86$

were obtained when 5 ml of 0.02 N ethanolic potassium hydroxide solution was added to the polymer solution and the excess was back-titrated potentiometrically with 0.02 N ethanolic hydrochloric acid. The potential drop around the equivalence point was about 45 mV. When, however, samples with carboxyl contents of 20–30 mequivs./kg were analysed, it was necessary to take at least 600 mg for analysis to obtain reproducible results. The minimum sample size as a function of the carboxyl content is given in Table II.

TABLE II

COOH content mequivs./kg	*minimum sample size mg*
50–90	200
30–50	400
20–30	600
15–20	800

Final results for some samples are given in Table III, in which the potentiometric results, y', are compared with the visual ones from Table I.

An increase in the sample size in the visual method was also examined; when 10 ml of benzyl alcohol is used not more than 400 mg of the polymer can be dissolved.

DISCUSSION

Application of the t-test to the $\bar{d}_i$ values of Table I reveals that they do not differ significantly from zero. This means that no systematic differences between the results of the respective methods can be proved. It must, therefore, be assumed that all three methods yield the same results when applied to one sample. The methods investigated are independent of each other, since different solvents are used and the equivalence points in the titrations are indicated in different ways. Because of this

TABLE III

CARBOXYL CONTENT OF POLYETHYLENE TEREPHTHALATE IN MEQUIVS. PER KG

Sample	*Visually*	*Potentiometrically*	*Sample size in the potentiometric method*	$d_4 =$
	x	y'		$\bar{x} - \bar{y}'$
1	22.5	21.5	600 mg	
	22.4	20.9		+1.4
	22.1	20.4		
3	79.8	81.9	200 mg	
	80.3	82.8		—0.9
	80.8	80.3		
4	25.8	23.4	600 mg	
	22.5	24.3		+0.4
	24.2	23.6		
7	58.3	59.7	200 mg	
	59.6	59.2		—0.4
	58.8	59.1		
mean, $\bar{d}_4$				+0.1
st. dev.	$s_x = 0.93$	$s_{y'} = 0.82$		$s_{d_4} = 1.01$

independence and the fact that the results obtained by the three methods do not differ significantly, the results found must be assumed to be accurate.

When the standard deviations of single determinations, *viz.* s_x, s_y and s_z are compared with the aid of the F-test, a significant difference can be detected on the 0.05-level only between s_x and s_y. It must therefore be assumed that the results of the potentiometric method, when applied to 2-g samples, are more precise than those of the visual method.

The potentiometric method can also be applied to smaller samples. From Table III it can be seen that when small samples of 200 to 600 mg are used in the potentiometric method, no systematic differences between the results of this method and those of the visual one can be detected. The standard deviation, $s_{y'}$, is somewhat higher than s_y, but does not differ significantly from the latter value.

The correction factor in the visual method was found to be 2.4 mequivs. per kg per min. This value does not agree with that mentioned by Pohl[5], who found 0.88 mequivs. per kg per min. When a sample contains 23 mequivs. of carboxyl groups per kg (Table I, samples 1, 2, 4 and 6) and the dissolution time is 2 min, the correction amounts to 4.8 mequivs. per kg, which is more than 20% of the amount to be determined. Such a correction must be considered inadmissibly large.

It should be remarked that the standard deviation s_x is of the same order of magnitude as that mentioned by Pohl[5], *viz.* 0.86 mequivs. per kg.

The potentiometric method has the advantage over the visual method that larger samples can be analyzed, so that the results are more precise and that no correction is required; however, it takes longer than the visual method. This disadvantage can be overcome by dissolving several samples simultaneously. In contrast to the HF titration, no special apparatus is required in the potentiometric method. For these reasons the latter is preferred to the visual and HF titration. In this investigation the HF titration was only used as a comparison method.

Finally, it may be remarked that the carboxyl groups in polyethylene terephthalate are dissociated to a relatively high extent. This is in accordance with the position of these groups in the molecules, bound as they are to the aromatic nuclei. Experimental evidence for this fact is obtained from the present results. The carboxyl groups can be sharply titrated to a visual end-point in a neutral solvent, *viz.* benzyl alcohol, whereas in the potentiometric titration in an acidic solvent a potential difference around the equivalence point of about 100 mV was observed at a concentration of $0.8 \cdot 10^{-3}$ to $3.2 \cdot 10^{-3}$ equivs./l.

RECOMMENDED PROCEDURE

Reagents

o-Cresol, c.p., (British Drug Houses) purified by distillation. Chloroform, c.p., purified by shaking with sodium carbonate solution, drying over anhydrous sodium sulphate, and distillation. Ethanolic potassium hydroxide solution, 0.1 (t_1) N, standardized against potassium hydrogen phthalate. Ethanolic potassium hydroxide solution, 0.02 N. Ethanolic hydrochloric acid, 0.02 (t_2) N.

Procedure

Weigh out 2 (p_1) g of ground polyethylene terephthalate in a 150-ml beaker to the nearest 0.005 g. Add 50 ml of a mixture of 70 g of *o*-cresol and 30 g of chloroform and heat to 90° until the sample has dissolved. This takes at most 30 min. Cool to room temperature, immerse the electrodes in the solution, stir and titrate potentiometrically with t_1 N ethanolic potassium hydroxide solution (v_1 ml). Carry out a blank by titrating 50 ml of the solvent with this titrant (v_0 ml).

If small samples are to be analyzed, weigh out 0.2–0.6 (p_2) g of the ground polymer to the nearest 0.001 g and dissolve as described above. After cooling add 5 ml of 0.02 *N* ethanolic potassium hydroxide solution, immerse the electrodes in the solution, stir and titrate potentiometrically with t_2 *N* ethanolic hydrochloric acid and record the first equivalence point (v_2 ml). Carry out a blank by adding 5 ml of 0.02 *N* ethanolic potassium hydroxide solution to 50 ml of the solvent and titrating potentiometrically with t_2 *N* ethanolic hydrochloric acid (v_3 ml).

Calculation

The sample contains:

$$\frac{1000(v_1 - v_0{}^1)t_1}{p_1} \text{ mequivs. of COOH per kg or } \frac{1000(v_3 - v_2)t_2}{p_2} \text{ mequivs. of COOH per kg.}$$

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SUMMARY

Three methods for the determination of carboxyl groups in polyethylene terephthalate are investigated, *viz.* (a) dissolution in hot benzyl alcohol, addition of chloroform, and titration with benzyl alcoholic potassium hydroxide solution to the phenol red end-point, (b) dissolution in a mixture of *o*-cresol and chloroform, and potentiometric titration with ethanolic potassium hydroxide solution, and (c) dissolution in a mixture of *o*-cresol, chloroform and acetone, and titration with ethanolic potassium hydroxide solution with HF-indication of the end-point.

The three methods yield the same results when applied to several samples of different carboxyl content. For several reasons the potentiometric method is preferred to the other two methods.

RÉSUMÉ

Trois méthodes pour le dosage des groupes carboxyles dans le téréphtalate polyaethylène ont été étudié, c'est à dire (a) par dissolution dans l'alcool benzylique, et addition de chloroforme suivi par une titration avec une solution benzylalcoolique de l'hydroxyde de potassium avec l'indicateur phenolrouge, (b) par dissolution dans une mélange de *o*-crésole et chloroforme suivi par une titration potentiométrique avec une solution aethanolique de l'hydroxyde de potassium et (c) par dissolution dans une mélange de *o*-crésole, chloroforme et acétone suivi par une titration ,,H.F." avec une solution aethanolique de l'hydroxyde de potassium.

Les trois méthodes donnent des résultats identiques quand ils sont appliquées aux échantillons avec un teneur carboxyle variable. La méthode potentiométrique est recommendée.

ZUSAMMENFASSUNG

Drei Methoden zur Bestimmung der Carboxylgruppen in Polyaethylenterephtalat wurden untersucht, und zwar (a) Lösen in heissem Benzylalkohol, Zugabe von Chloroform und Titration mit benzylalkoholischer Kaliumhydroxydlösung auf Phenolrot, (b) Losen in einem Gemisch von *o*-Kresol und Chloroform und potentiometrische Titration mit aethanolischer Kaliumhydroxydlösung und (c) Lösen in einem Gemisch von *o*-Kresol, Chloroform und Aceton, und H.F.-Titration mit aethanolischer Kaliumhydroxydlosung.

Die drei Methoden geben dieselben Ergebnisse, wenn sie auf mehrere Muster mit verschiedenem Carboxylgehalt angewandt wurden. Von den genannten Methoden wird die potentiometrische Methode bevorzugt.

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DOSAGE POLAROGRAPHIQUE DE LA TYROSINE, DU TRYPTOPHANE ET DE LA PHÉNYLALANINE EN PRÉSENCE LES UNS DES AUTRES

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Nous avons proposé dans diverses publications[1], des méthodes de dosage polarographique de ces trois acides aminés. Ces derniers se nitrent facilement, à l'encontre de la plupart des autres et les dérivés que l'on obtient donnent des sauts polarographiques parfaitement dessinés dont le potentiel $E_{\frac{1}{2}}$ est toujours inférieur à 1 V. Dans ce travail, pour rendre la méthode encore plus spécifique, nous avons cherché à doser chacun d'eux en présence des deux autres. La plupart des autres acides aminés ne se nitrent pas dans ces conditions et par conséquent ne gênent pas. Dans chaque cas nous donnerons la précision et la sensibilité de la méthode.

I. Dosage de la tyrosine en présence de tryptophane et de phénylalanine

La tyrosine traitée par l'acide nitrique 0.15 N, à l'ébullition pendant 2 h, donne un dérivé nitré qui se réduit sur la goutte de mercure et donne un polarogramme dont le $E_{\frac{1}{2}}$ vaut 0.64 V et dont la hauteur est, dans des limites déterminées, rigoureusement proportionnelle à la concentration. La présence de dérivés sulfurés de la forme -SH (cystéine) de même que celle du tryptophane rend la nitration impossible dans les conditions indiquées. Tous les essais que nous avons effectués pour induire la réaction de nitration, sans augmenter la concentration d'acide nitrique sont restés vains. L'addition d'un cristal de nitrite de sodium provoque bien une réaction mais les sauts polarographiques qui en résultent ne correspondent plus à la concentration de tyrosine. Une séparation s'avère donc indispensable. Or il se trouve que l'acétate de mercure précipite l'un et l'autre de ces deux composés. Cette réaction est lente mais quantitative, les produits de solubilité étant très faibles; la méthode s'applique aussi au dosage de très petites quantités de tyrosine. Pour accélérer la précipitation, il est bon de travailler à 50-60°, ce qui a l'avantage de donner un précipité plus aisément filtrable. Les traces de mercure qui restent en solution ne gênent pas la détermination. Une difficulté se présente lorsque le précipité tryptophane-mercure est trop abondant. En effet il adsorbe des quantités non négligeables de tyrosine. C'est pourquoi nous proposons d'utiliser un back-carrier qui sera adsorbé à la place de la tyrosine. Nous avons montré que la phénylalanine convient particulièrement bien car elle ne gêne pas le dosage de la tyrosine, même en grand excès et qu'elle est plus fortement adsorbée que cette dernière sur le précipité tryptophane-mercure. En effet nous avons pu montrer que la phénylalanine était capable de remettre en solution la tyrosine préalablement adsorbée par le précipité. Nous avons donc procédé de la façon suivante:

Une solution contenant 0.0119 g de tyrosine et 0.080 g de tryptophane a été divisée en deux portions et la précipitation a été faite. On a ensuite ajouté 0.070 g de phénylalanine dans l'une des solutions qui a été chauffée et bien agitée. Les polarogrammes effectués après nitration ont montré que la solution ayant reçu la phénylalanine donne un saut de 7% plus élevé que la solution témoin, il semble donc bien se produire en présence de phénylalanine une certaine remise en liberté de la tyrosine.

Nous avons cherché la quantité minimum de phénylalanine à ajouter à une solution renfermant des quantités déterminées de tyrosine et de tryptophane, pour que ce dernier ne gêne pas le dosage de la tyrosine.

TABLEAU I

Tyrosine (mg)	*Tryptophane (mg)*	*Phénylalanine (mg)*	*Saut μA*	*Mol. Phényl. / Mol. Trypt.*
10.8	80	40	10.9	0.62
10.8	80	60	11.5	0.93
10.8	80	80	11.4	1.24
10.8	80	120	11.4	1.85

Nous remarquons que la première prise présente un saut un peu faible, mais que les suivantes donnent par contre des hauteurs pratiquement identiques. Ce résultat est parfaitement plausible, car les poids moléculaires de la phénylalanine et du tryptophane étant respectivement de 165.19 et 204.2, le rapport moléculaire 1/1 correspond à 64.7 mg de phénylalanine pour 80 mg de tryptophane. En dessous de cette limite, la quantité de phénylalanine ne semble pas être suffisante pour empêcher une certaine adsorption de la tyrosine.

MODE OPÉRATOIRE

a. On place la prise contenant environ 10 à 20 mg de tyrosine dans un tube à centrifuger et on la dissout dans 30 ml d'acide nitrique 0.15 *N*. On ajoute à celle-ci une quantité de phénylalanine correspondant aux 3/4 au moins du poids de trytophane. Si celui-ci n'est pas connu, mettre un bon excès (on peut contrôler en effectuant les mêmes opérations sur une prise parallèle contenant davantage de phénylalanine). Tiédir à 50–60° pour faciliter la mise en solution.

b. Ajouter une quantité de solution d'acétate mercurique (à 2% dans l'acide nitrique 0.15 *N*) telle, que la solution devienne totalement opaque au moment de l'adjonction, plus un petit excès de 0.5 ml environ.

c. Placer les tubes à centrifuger dans un bécher d'eau maintenue à environ 60° et laisser reposer ainsi à chaud pendant une à deux heures.

d. Centrifuger environ 1/4 d'heure et, si nécessaire, filtrer sur double filtre pour enlever le dernier trouble éventuel. Transvaser dans un cylindre gradué ou dans un flacon jaugé pour amener à un volume connu et prélever une partie aliquote de cette solution (20 ou 25 ml).

e. Placer cette prise dans un erlenmeyer rodé avec réfrigérant à reflux et ajouter 20 ml d'acide nitrique 0.15 *N* ainsi que quelques cristaux de nitrite de sodium. Porter à ébullition durant deux heures, puis refroidir sous l'eau courante.

f. Neutraliser ensuite par l'hydroxyde de potassium à 20% en contrôlant au moyen de papier indicateur universel. Placer dans un flacon jaugé de 50 ml et compléter par de l'eau bidistillée.

g. Prélever 5 à 7 ml de cette solution, ajouter 2 ml de solution tampon de pH 5* et compléter à 10 ml. Chasser l'oxygène et polarographier à la sensibilité convenable.

On effectue les mêmes opérations sur une prise à laquelle on a ajouté une quantité connue de tyrosine témoin (étalon interne).

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* 51.5 ml de Na_2HPO_4 0.2 *M* + 48.5 ml d'acide citrique 0.1 *M*.

Des essais de contrôle ont été faits et les résultats suivants ont été enregistrés au moyen d'un polarographe Sargent XXI et à la sensibilité de 0.080 μA/mm.

TABLEAU II

Tyrosine (mg)	*Tyrosine ajoutée*	*Tryptophane (mg)*	*Phénylalanine (mg)*	*Saut µA*	*Tyrosine trouvée (mg)*
9.3	—	80	60	5.76	9.5
9.3	4.4	80	60	8.43	
16.2	—	50	40	10.58	16.05
16.2	5.2	50	40	14.01	

APPLICATIONS

Dosage de la tyrosine dans l'albumine du sang

Nous avons dosé la tyrosine sans hydrolyse préalable de l'albumine, afin d'obtenir la teneur en tyrosine „libre", puis nous avons effectué la même détermination sur la tyrosine liée aux chaines peptidiques. Dans ce dernier cas, elle est libérée par l'un des procédés d'hydrolyse classique.

On utilise principalement le traitement par ébullition à reflux en présence d'hydroxyde de sodium, d'hydroxyde de potassium ou d'acide sulfurique avec adjonction éventuelle de certains sels minéraux tels que le chlorure d'étain.

La littérature donne les chiffres suivants, concernant les divers procédés d'hydrolyse:

Traitements et pertes moyennes indiquées par les auteurs:

BLOCK ET BOLLING (1943)[2]. Traitement par NaOH 5 *N*; Durée 5 h; Température entre 115 et 125°; Pertes de tyrosine: 11 à 17%.

LUGG (1938)[2]: NaOH 5 *N*; Durée de 20 à 30 h; Température 100°; Pertes nulles de tyrosine.

JORPS (1932)[2]: NaOH 5 *N*; Durée de 14 à 18 h; Température 100°; Pertes de tyrosine = 0 à 9%.

La majorité des auteurs considèrent l'hydrolyse alcaline par l'hydroxyde sodium, eventuellement l'hydroxyde de potassium, comme étant la meilleure pour le dosage de la tyrosine. Nous conformant à cette manière de voir, nous avons appliqué la méthode de BOLLING ET BLOCK. C'est la meilleure bien que la tyrosine ne soit pas entièrement libérée. L'erreur due aux pertes se maintient dans une limite raisonnable, ce qui permet l'utilisation d'un facteur correctif (1.18) déterminé sur un grand nombre d'analyses. La durée de ce traitement n'est pas exagérée.

a. Dosage de la tyrosine totale. Une prise d'albumine d'environ 30 mg est placée dans un erlenmeyer rodé en présence de 20 ml d'hydroxyde de sodium 5 *N*. On chauffe à reflux entre 115 et 125° pendant 5 h au moyen d'un bain d'huile ou sur une plaque chauffante électrique.

Après refroidissement, on neutralise par de l'acide nitrique concentré et transvase dans un cylindre gradué. On ajoute ensuite une quantité d'acide nitrique telle que la concentration finale de l'acide soit de 0.15 *N*. (Il est inutile de faire cette acidification avec grande précision, les essais ont montré que de petits écarts n'influencent pas la hauteur des vagues polarographiques).

On place à nouveau la solution dans l'erlenmeyer rodé et on fait bouillir à reflux durant deux heures. Les essais qualitatifs préliminaires ont montré qu'il ne se produit aucune précipitation en présence d'acétate mercurique, il a donc été inutile dans ce cas, d'utiliser ce réactif.

Après refroidissement, on porte la solution au volume de 50 ml dans un flacon jaugé, on en prélève 7 ml auxquels on ajoute 2 ml de la solution tampon de pH 5 et on complète à 10 ml. On polarographie après avoir chassé l'oxygène.

On procède de manière analogue avec des prises contenant une quantité connue de tyrosine pure servant d'étalonnage interne.

Nous avons enregistré les valeurs suivantes:

TABLEAU III

Albumine (Prise en mg)	*Tyrosine ajoutée (mg)*	*Saut* μA	*Tyrosine trouvée (mg)*	*Résultat* %
28	—	0.62	1.24	4.4
28	8.0	5.52		
23	—	0.58	0.985	4.3
23	7.0	4.90		

Les chiffres de la colonne 4 ont été calculés en tenant compte du facteur correctif 1.18.
Les chiffres de la colonne 5 indiquent la teneur de l'albumine en tyrosine.

La qualité des sauts est très bonne et il est possible de travailler à une sensibilité encore plus grande que celle de 0.090 μA/mm qui a été utilisée, ce qui facilite la mesure des hauteurs.

b. Dosage de la tyrosine libre. Comme il a été dit plus haut, nous avons fait parallèlement un essai de nitration sur l'albumine non hydrolysée, de manière à obtenir une courbe comparative. Nous constatons que dans ce cas, il ne se produit pratiquement pas de saut. Seule une faible vague, à peine dessinée, marque l'emplacement du saut de la tyrosine. Cette légère ondulation, parfaitement reproductible, est très probablement due à une petite quantité de tyrosine rendue libre par une faible hydrolyse lors de la préparation de l'albumine.

Remarque: Les valeurs que nous avons obtenues pour la teneur de l'albumine en tyrosine sont en accord avec celle que l'on peut trouver dans la littérature.

(Documenta Geigy, Tables scientifiques[3] = 4.66%; BLOCK ET BOLLING[2] = entre 3.9 et 7.3%; D. E. DUGGAN ET S. UNDENFRIEND[4] = 5.5% pour l'albumine de sang de bovidés).

Ces essais nous ont permis de contrôler l'application de la méthode de dosage à un mélange complexe, en éprouvant la technique opératoire. Pour les mesures quantitatives rigoureuses, nous utiliserons un produit de synthèse dont la composition est exactement connue.

Dosage de la tyrosine dans la N-carbobenzoxy-S-benzyl-L-cystéinyl-L-tyrosine

Nous avons procédé à l'analyse d'un produit de synthèse aimablement mis à notre disposition par MM. BOISSONNAS *et al.*[5] dont la composition est exactement connue. Il s'agit de la N-carbobenzoxy-S-benzyl-L-cystéinyl-L-tyrosine; la molécule de ce composé peptidique a un poids de 508.57. La tyrosine s'y trouve donc dans le rapport 181/508.6 = 0.356.

Les dosages ont été conduits de la manière suivante:

On effectue deux prises traitées de façon identique, sauf que l'une d'elle reçoit une quantité étalon de tyrosine pure. On ajoute 10 ml d'hydroxyde de sodium 5 *N* et on chauffe pendant 5 h à environ 120°. Après refroidissement, on neutralise par de l'acide nitrique concentré, on amène à 25 ml dans un cylindre gradué, tout en ajoutant 2.5 ml d'acide nitrique 1.5 *N* et 1 ml de solution d'acétate mercurique à 2% dans l'acide nitrique 0.15 *N*. On transvase dans une éprouvette à centrifuger et on centrifuge jusqu'à obtention d'une solution tout à fait limpide, ce qui ne nécessite d'ailleurs que quelques minutes. On décante soigneusement et on prélève 20 ml que l'on place dans un erlenmeyer rodé. On ajoute encore 10 ml d'acide nitrique 0.15 *N* et un ou deux cristaux de nitrite de sodium, puis on fait bouillir à reflux durant 2 h. L'analyse se termine ensuite de la manière habituelle (voir page 2).

Les résultats suivants ont été obtenus:

TABLEAU IV

Prises d'hydrolysat (mg)	*Tyrosine (mg) valeur théorique*	*Tyrosine étalon (mg)*	*Saut µA*	*Tyrosine trouvée (mg)*	*Ecarts %*
6.5	1.97	—	0.755	1.88	—4.6
6.5	1.97	5.2	2.84		
6.5	1.97	—	0.80	2.03	+3
6.5	1.97	5.2	2.84		
8.9	2.70	—	0.91	2.75	+1.85
8.9	2.70	5.3	2.67		
5.5	1.67	—	0.578	1.63	—2.5
5.5	1.67	5.9	2.675		

Nous voyons d'après ces chiffres que les écarts se maintiennent dans une limite raisonnable, compte tenu de la petitesse des prises, rendue nécessaire par la faible quantité de produit disponible.

II. Dosage du tryptophane en présence de tyrosine et de phénylalanine

a. Dosage du tryptophane seul ou en présence de phénylalanine. Le tryptophane ne se nitre pas avec l'acide nitrique 0.15 *N* utilisé pour le dosage de la tyrosine. Par contre l'acide 1.5 *N* donne un composé qui se réduit au polarographe au pH 5, comme dans le cas de la tyrosine. Les sauts sont parfaitement reproductibles et bien dessinés. La phénylalanine ne gêne en aucune façon; il faut, pour la nitrer, des conditions beaucoup plus énergiques.

La vague du tryptophane, au pH 5, se situe dans le voisinage de celle de la tyrosine à 0.75 V (par rapport à la surface mercure/solution). Le mode opératoire est semblable à celui mis en oeuvre pour le dosage de la tyrosine:

On utilise 40 ml d'acide nitrique 1.5 *N* pour une prise de l'ordre de 10 à 30 mg de tryptophane.

On nitre par ébullition à reflux durant deux heures.

On neutralise par l'hydroxyde de potassium à 20%.

On amène à 50 ml. On prélève une partie aliquote que l'on additionne de solution tampon de pH 5 (phosphate disodique/acide citrique). On polarographie cette solution.

Les valeurs suivantes ont été obtenues en travaillant à la sensibilité de 0.080 µA/mm.

TABLEAU V

Tryptophane (mg)	*Concentration (mg/l)*	*Saut µA*	*K mg/l/µA*
11.0	77	5.68	13.55
15.2	106.4	7.44	14.3
19.3	135.2	9.12	14.8
22.4	156.8	10.16	15.65

Note. La valeur de K est régulièrement croissante car la droite d'étalonnage tracée à l'aide de ces points ne passe pas tout à fait par l'origine.

Les résultats sont identiques que le tryptophane soit ou non en présence de phénylalanine.

b. Dosage du tryptophane en présence de tyrosine. Le dosage différentiel n'est pas possible, il y a interaction de ces composés au cours de la réaction qui fait que les sauts polarographiques ne sont ni reproductibles, ni proportionnels aux concentrations de ces composés. L'augmentation de la concentration de l'acide nitrique ne donne pas de résultats meilleurs. Nous avons tenté de détruire la tyrosine, plus sensible que le tryptophane à l'oxydation. On y parvient avec le permanganate de potassium par exemple, mais cet oxydant détruit partiellement le tryptophane, il n'est par conséquent pas utilisable.

Ceci a d'autre part été montré dans la thèse de R. GUERNE[6] qui indique que le saut du tryptophane est diminué d'environ 70% (il est probable que le saut est alors donné par les produits résultant de l'oxydation). Nous avons pensé pouvoir utiliser, pour cette destruction, l'oxygène par barbotage dans la solution chaude. Même après plus d'une heure, il nous a été impossible de faire disparaître le saut de la tyrosine. L'emploi de l'eau oxygénée n'a pas donné de résultat. En conclusion, il ne nous a pas été possible de détruire la tyrosine en présence de tryptophane sans provoquer des interférences.

Etant donné ces résultats, une séparation s'imposait. Pour cela, nous avons utilisé l'acétate de mercure(II) qui nous a déjà permis d'éliminer l'effet gênant du tryptophane (voir page 1).

Comme il a été dit précédemment, le précipité tryptophane–mercure est insoluble dans l'acide nitrique dilué, même à chaud. Mais si on le met en suspension dans l'acide nitrique 1.5 *M* et qu'on fasse bouillir à reflux, le précipité prend une teinte jaune plus foncée, puis se dissout en quelques minutes. On obtient finalement une solution jaune tout à fait limpide dans laquelle on peut doser le tryptophane. Des essais quantitatifs, conduits avec soin, ont été entrepris sur des solutions de cet acide aminé.

On place dans un tube à centrifuger l'échantillon de tryptophane, on le dissout dans l'acide nitrique 0.15 *N*. On introduit une solution d'acétate mercurique à 2% (dans NO_3H 0.15 *N*) en quantité telle qu'il se produise presque immédiatement une précipitation jaune pâle opaque (un excès est sans importance). On place ensuite le tube à centrifuger dans un bécher d'eau chaude servant de bain-marie qu'on maintient à environ 60° pendant 2 h, de manière à obtenir une précipitation totale.

L'addition d'une nouvelle quantité d'acétate mercurique ne doit plus provoquer de trouble, on s'assure ainsi que la précipitation a été quantitative. Dans ces conditions, la solution surnageante n'est pas colorée en jaune et sa polarographie ne présente pas de saut, même si on le porte à ébullition à reflux.

Le précipité obtenu est centrifugé durant 5 à 10 min jusqu'à ce que la solution soit tout à fait limpide.

On l'introduit ensuite dans un erlenmeyer rodé en ajoutant 20 ml d'acide nitrique 1.5 *N* et on fait bouillir à reflux durant 2 h. Après refroidissement, on neutralise par une solution d'hydroxyde de potassium à 20%, on transvase dans un flacon jaugé pour compléter à 50 ml par de l'eau bidistillée et on prélève 7 ml de cette solution. La prise est additionnée de 3 ml de solution tempon de pH 5 (phosphate disodique–acide citrique), on en élimine l'oxygène et on polarographie.

Nous donnons ci-dessous les valeurs obtenues pour une série d'analyses:

TABLEAU VI

Tryptophane (mg)	*Concentration (mg/l)*	*Saut* μA	*Ecarts* %
7.2	72	4.90	0
12.6	126	8.36	+5
18.8	188	11.4	—0.8
21.7	217	13.0	0

On peut voir d'après le tableau ci-dessus que l'utilisation du précipité tryptophane–mercure(II) comme moyen de séparation se présente de manière favorable.

Remarque: Au cours de la nitration, le mercure qui a servi à la précipitation du tryptophane est libéré, mais au moment de la neutralisation par l'hydroxyde de potassium, il précipite à nouveau de façon pratiquement quantitative de sorte qu'il ne gêne pas la détermination polarographique.

c. Dosage du tryptophane en présence de tyrosine et de phénylalanine. Nous allons donner maintenant le mode opératoire d'un dosage du tryptophane en présence de tyrosine et de phénylalanine.

La présence de phénylalanine ne nécessite aucune précaution spéciale lors des opérations de dosage. Par contre, il est nécessaire que la séparation de la tyrosine soit faite avec grand soin.

MODE OPÉRATOIRE

a. Placer la prise contenant de 5 à 30 mg de tryptophane et une quantité suffisante de phénylalanine (en ajouter si nécessaire; voir mode opératoire page 2) dans un tube à centrifuger; y ajouter 20 à 30 ml d'acide nitrique 0.15 *N*. Dissoudre par léger chauffage.

b. Introduire une solution d'acétate mercurique à 2% (dans l'acide nitrique 0.15 *N*) jusqu'à obtention d'un trouble jaune pâle opaque.

c. Maintenir au bain-marie à environ 60° pendant 1 à 2 h, de manière à assurer une précipitation complète.

d. Centrifuger le précipité formé et décanter la solution lorsque celle-ci est tout à fait limpide. Effectuer un lavage au moyen d'acide nitrique 0.15 *N* (environ 20 ml) en remettant le précipité en suspension, puis centrifuger à nouveau.

e. Placer le composé tryptophane–mercure(II) dans un erlenmeyer rodé de 100 ml en ajoutant 30 ml d'acide nitrique 1.5 *N*. Chauffer à ébullition à reflux durant 2 h.

f. Après refroidissement, neutraliser par l'hydroxyde de potassium à 20% et centrifuger le léger trouble qui se forme.

g. Compléter à 50 ml par de l'eau bidistillée, prélever 5 à 7 ml que l'on amène à 10 ml au moyen de la solution tampon de pH 5.

h. Chasser l'oxygène par un courant d'azote pur pendant 8 à 10 min, puis polarographier.

Remarque : Après la seconde décantation (opération d), il est préférable, afin d'éviter un transvasage du précipité, d'introduire l'acide nitrique 1.5 *N* directement dans le tube à centrifuger contenant le composé tryptophane–mercure(II) propre. On y commence le chauffage au moyen d'un bain-marie bouillant de manière à ce que le précipité se dissolve. La solution est ensuite transvasée quantitativement dans l'erlenmeyer rodé pour poursuivre la nitration (opération e). De cette manière on évite toute perte de produit; celui-ci est en effet assez adhérent aux parois et sa récupération quantitative nécessite des soins.

Nous donnons ci-dessous, les résultats de différentes analyses faites sur des prises contenant des quantités variables de tyrosine et de phénylalanine.

TABLEAU VII

Prises (mg)			*Tryptophane ajouté (mg)*	*Saut µA*	*Tryptophane trouvé (mg)*	*Ecarts %*
Tryptophane	*Tyrosine*	*Phénylalanine*				
9.0	15	15	—	5.69	8.8	—2.2
9.0	15	15	4.2	8.41		
7.9	30	30	—	4.98	7.6	—3.8
7.9	30	30	2.2	6.42		
8.0	20	20	—	5.42	8.4	+5
8.0	20	20	5.1	8.70		

Nous voyons d'après ces résultats que la marge d'erreur que l'on observe est de ±5%. Elle est supérieure à celle du dosage de la tyrosine (±3%). Mais il faut tenir compte du fait que l'on a maintenant un dosage comprenant une précipitation suivie de lavage et de transvasage. Les opérations effectuées sur un précipité sont presque toujours moins précises que celles ne nécessitant que des manipulations de solutions

III. Dosage de la phénylalanine en présence de tyrosine et de tryptophane

Le dosage de la phénylalanine a déjà été décrit[6]. Rappelons dans les grandes lignes la méthode utilisée.

Les prises sont traitées dans de petites éprouvettes à fond plat, au moyen de 0.5 ml d'acide nitrique 10 *N*. On porte à ébullition sur une plaque chauffante électrique durant 1 h 30 min tout en assurant un reflux convenable au moyen d'un récipient contenant de l'eau froide. On neutralise en présence de rouge de méthyle, substance qui intervient ensuite au cours du dosage polarographique comme suppresseur de maximum. On polarographie la solution tamponnée au pH 6 (phosphate disodique–acide citrique). Les écarts sont de l'ordre de 2.5% pour les concentrations de l'ordre du milligramme.

Remarque : Lors de l'application de cette méthode, nous avons préféré utiliser un bain d'huile pour assurer le chauffage des éprouvettes. La température de 120° environ donne des résultats comparables à ceux obtenus en travaillant directement sur la plaque électrique à la température d'ébullition de la solution. Comme cette température est relativement élevée, il se produit fréquemment des projections qui risquent de causer des pertes de substances (l'emploi de pierres à ébullition pour d'aussi faibles volumes n'est pas pratique). A 120°, la solution n'est pas encore en ébullition et il n'y a par conséquent pas de projections possibles. Le bain d'huile nous assure d'autre part une température uniforme entre les divers tubes à essai en cours de traitement.

Le dosage n'est évidemment pas possible en présence de tyrosine et de tryptophane qui sont partiellement détruits par cette nitration et dont les résidus perturbent la mesure polarographique.

Une solution de tyrosine traitée par le permanganate de potassium jusqu'à coloration rose persistante puis décoloration par l'eau oxygénée peut être soumise deux heures à l'action de l'acide nitrique sans présenter le moindre saut polarographique. On peut donc en conclure que cet acide aminé est entièrement oxydé et que les produits d'oxydation qui en résultent ne peuvent être nitrés dans ces conditions.

Nous avons traité de la même manière une solution de phénylalanine et nous avons pu voir que la hauteur du saut polarographique produit après traitement par HNO_3 10 N n'est pas modifiée. Nous préférons utiliser pour l'oxydation une solution concentrée de permanganate (la solution saturée est à 6.4% environ) plutôt que des cristaux dont l'action est plus lente.

Le tryptophane soumis à l'action du permanganate, même à chaud et en présence de nitrate d'argent laisse subsister un saut, il ne peut donc être éliminé de cette manière. Cependant, nous avons vu qu'il est facile de le précipiter et c'est la combinaison d'une oxydation et d'une précipitation qui rendra possible le dosage de la phénylalanine en présence des deux autres acides amiéns. Pour l'élimination du tryptophane, la méthode qui consiste à le précipiter directement par l'acétate de mercure est longue et délicate et les résultats manquent de précision. Nous avons constaté qu'il est préférable de procéder d'abord à la nitration du mélange et d'éliminer ensuite seulement le tryptophane.

Elimination de la tyrosine et du tryptophane après nitration

Nous avons vu précédemment que le précipité que donne le tryptophane en présence de mercure commence à se dissoudre au moment de l'ébullition de l'acide nitrique 1.5 N. Mais si l'on amène une solution de tryptophane nitré à un pH légèrement acide (pH compris entre 2 et 3), on s'aperçoit qu'il se forme, en présence d'un excès de mercure, un précipité jaune orange de tryptophane nitré. (La solution ne doit être ni trop acide, ni neutre). Ce qui montre que la précipitation au tryptophane peut se faire aussi bien après qu'avant la nitration.

MODE OPÉRATOIRE

On place la prise contenant un mélange des trois amino-acides dans un petit tube à fond plat (la pesée se fait directement dans le tube). On ajoute 1 ml d'acide nitrique 10 N. On place dans un bain d'huile à 120° pendant 1 h 30 min. Le reflux est assuré par un récipient contenant de l'eau froide, placé sur l'ouverture du tube.

Après refroidissement, on ajoute de l'hydroxyde de potassium à 20% au moyen d'un compte-gouttes très effilé, jusqu'à neutralisation (visible par le virage de la teinte à l'orange). On transvase ensuite dans un tube à centrifuger en ajoutant environ 10 ml d'eau bidistillée.

On réacidifie légèrement avec de l'acide nitrique dilué de manière à obtenir un pH compris entre 2 et 3, puis on ajoute 5 ml de solution d'acétate mercurique à 2%. On place dans un bain-marie à environ 60° pendant 1 à 2 heures; on centrifuge ensuite pendant quelques minutes, jusqu'à obtention d'une solution limpide.

On décante soigneusement dans un deuxième tube à centrifuger, on ajoute 2 ml d'acide nitrique 0.1 N à la solution ainsi que 2 ou 3 gouttes de nitrate d'argent à 10%, puis une solution concentrée de permanganate de potassium jusqu'à coloration rose persistante (de 2 à 3 ml environ). On place au bain-marie à 60–80° pendant 15 minutes. (La présence de nitrate d'argent est nécessaire pour que l'oxydation se fasse dans le temps indiqué; la tyrosine subsiste bien plus longtemps en l'absence de ce réactif. La coloration rose finale doit être bien nette et dominer la couleur brune due au bioxyde de manganèse; si elle tend à disparaître pendant le chauffage, rajouter un peu de permanganate de potassium).

Après oxydation, on ajoute quelques gouttes d'eau oxygénée pour détruire l'excès de permanganate.

La solution est ensuite transvasée dans un cylindre gradué et neutralisée par de l'hydroxyde de potassium à 20%; le mercure, le manganèse et l'argent précipitent. On amène ensuite par de l'eau bidistillée à un volume bien déterminé et on verse dans un nouveau tube le liquide contenant le dépôt. On centrifuge quelques minutes jusqu'à obtention d'une solution limpide de teinte légèrement jaune (la teinte du dérivé nitré de la phénylalanine est faible comparée à celle que donnent les autres amino-acides).

On prélève une partie aliquote aussi grande que possible, que l'on amène à 50 ml dans un flacon jaugé. On prend 7 ml de cette solution et on complète à 10 ml au moyen de la solution tampon de pH 5.

On chasse l'oxygène par un courant d'azote pur pendant 8 à 10 min, puis on polarographie.

Les essais ont montré qu'il ne se produit pas de pertes de phénylalanine au cours du traitement. Il se produit en fait une faible perte par adsorption sur le tryptophane précipité, mais comme nous l'indiquons plus loin, nous avons constaté, dans ces conditions, une nitration plus forte de la phénylalanine, ces deux phénomènes semblent se compenser partiellement.

Nous avons obtenu par exemple les chiffres suivants, avec des prises contenant des quantités variables de phénylalanine.

TABLEAU VIII

Prises (mg)			*Saut*	*Phénylalanine trouvée*	*Ecarts*
Phénylalanine	*Tyrosine*	*Tryptophane*	*μA*	*(mg)*	*%*
7.9	20	20	3.16	8.1	+2.5
9.0	20	20	3.52	8.9	—1.1
9.4	20	20	3.61	9.2	—2.1
3.5	30	30	1.30	3.3	—6
6.6	30	30	2.91	6.75	+2.3
10.1	30	30	4.06	10.3	+2

Nous voyons que les erreurs que l'on commet dans le dosage de la phénylalanine en présence de tyrosine et de tryptophane sont acceptables, elles ne dépassent pas ±5%.

Mais nous avons fait une constatation importante. Si l'on effectue une nitration de la phénylalanine pure dans les mêmes conditions de température et de durée, on obtient régulièrement un saut d'environ 10% plus petit que dans le cas où l'on est en présence de tyrosine et de tryptophane. Tout ce passe comme si la phénylalanine, en présence de ces deux acides aminés, subissait une nitration induite plus énergique que lorsqu'elle est seule.

Le même phénomène se produit en présence de nitrite de sodium. Ce sel, que l'on n'ajoute pas lorsqu'on travaille avec des concentrations acides aussi fortes, a cependant, une influence certaine sur le déroulement de la nitration. Nous avons observé en effet que:

a. En présence de nitrite, la réaction s'amorce rapidement et la coloration jaune apparaît en quelques minutes. La coloration finale est un peu plus intense que celle que l'on obtient lors du traitement de phénylalanine pure. Le saut polarographique est également un peu plus élevé.

b. Dans le cas de la phénylalanine nitrée par l'acide nitrique 10 *N* pur, la réaction se produit très progressivement et la coloration finale n'est atteinte qu'insensiblement.

Nous ne pouvons affirmer cependant que, quantitativement, l'induction produite par le nitrite est comparable à celle due à la tyrosine ou au tryptophane. Il est donc préférable de procéder à un étalonnage interne de la manière habituelle.

Remarque : Si, au cours des opérations, l'oxydation de la tyrosine ou la précipitation du tryptophane n'a pas été faite correctement. On s'en aperçoit par le fait que les sauts se trouvent déformés.

Dosage par étalonnage interne

En procédant de la manière qui a été décrite plus haut (voir page 9), nous avons effectué quelques dosages par étalonnage interne de la phénylalanine en présence de quantités cinq fois plus fortes de tyrosine et de tryptophane.

Nous avons obtenu les valeurs suivantes

TABLEAU IX

Phénylalanine (mg)	*Phénylalanine ajoutée (mg)*	*Saut* μA	*Phénylalanine trouvée (mg)*	*Ecarts* %
5.7	—	1.38	5.9	+3.5
5.7	5.6	2.79		
4.0	—	0.90	3.8	—5
4.0	5.9	2.30		
4.1	—	0.945	4.0	—2.5
4.1	5.7	2.29		

Pour que le dosage soit exact, il est bien évident qu'il est nécessaire d'éliminer soigneusement les deux amino-acides gênants. Avec un excès de mercure et si l'on a attendu un temps suffisant, l'élimination du tryptophane est complète. En ce qui concerne l'oxydation de la tyrosine, on doit, si l'on a des doutes, faire une nouvelle oxydation à chaud de quelques minutes. Si la première oxydation a été totale, on retrouve un saut exactement identique, compte tenu de la petite dilution faite par l'introduction des différents réactifs nécessaires.

IV. Dosage du tryptophane, de la tyrosine et de la phénylalanine en présence les uns des autres

a. La prise contenant les substances à doser est mise en solution dans l'acide nitrique 0.15 *M*. On effectue la précipitation du tryptophane et on dose la tyrosine dans la solution résultante (voir page 2).

b. Le précipité renfermant le tryptophane est dissous dans l'acide nitrique 1. 5 *M*. On continue ensuite le dosage selon la méthode habituelle (voir page 7).

c. Sur une deuxième prise de substance, on procède à la nitration directe avec l'acide nitrique 10 *M* ; on précipite le tryptophane et on oxyde la tyrosine de sorte que le saut résultant donne la teneur en phénylalanine (voir page 9).

Chaque polarogramme doit avoir la forme correspondante à celle des produits purs. Les interférences se signalent immédiatement par des courbes irrégulières, des inflexions dans le tracé des sauts etc. Elles sont la preuve d'une mauvaise séparation ou de la présence de substances gênantes.

Application à l'analyse d'une peptone

Nous avons pu nous procurer auprès de la maison Hoffmann-La Roche, un produit dont la teneur en acides aminés qui nous intéresse est approximativement connue. Cette maison a utilisé pour ses dosages des méthodes biologiques.

Le produit est un hydrolysat de caséine (Peptone „Roche'') dont les teneurs suivantes nous ont été indiquées: Tyrosine = 2.4%; Tryptophane = 2.1%; Phénylalanine = 10.9%. (L'ordre de grandeur de la précision de ces valeurs n'a pu nous être donné).

Cette peptone contient en outre les acides aminés suivants (en %): Alanine = 2.5, Arginine = 3.1, Acide aspartique = 12.5, Cystine = 1.2, Acide glutamique = 16.5, Histidine = 2.5, Isoleucine = 8.7, Leucine = 8, Méthionine = 5.5, Proline = 1.9, Sérine = 8, Thréonine = 6.3, Valine = 10.5, Lysine = 8.

L'analyse a été conduite comme il a été indiqué plus haut. Malgré la complexité de la substance étudiée, les réactions se déroulent normalement et l'on obtient des courbes polarographiques de très bonne qualité.

a. Dosage du tryptophane. Les dosages en ce qui concerne le tryptophane ont donné les résultats suivants:

TABLEAU X

Peptone (mg)	*Tryptophane témoin (mg)*	*Saut µA*	*Valeur trouvée (mg)*	%
200	—	0.945	4.05	2.02
200	6.2	2.36		
200	9.3	3.11		
200	—	0.90	4.1	2.05
200	8.0	2.61		
			Valeur indiquée	2.1

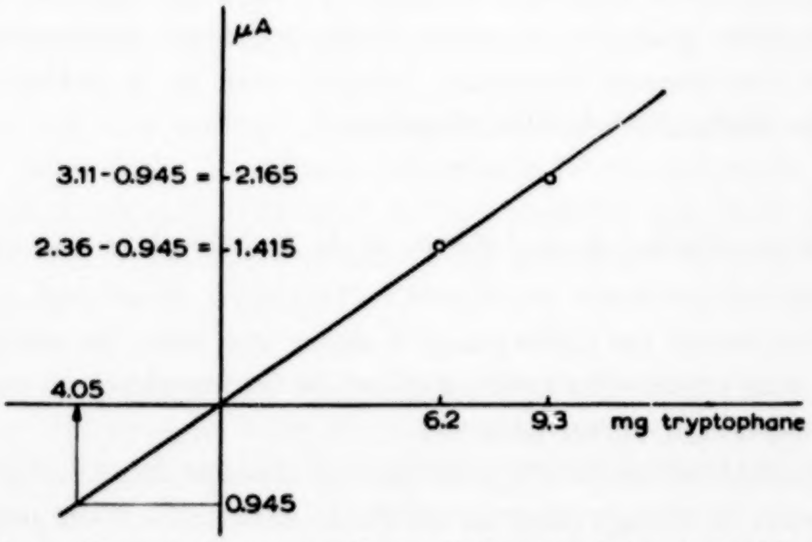

Fig. 1. Dosage du tryptophane; étalonnage interne double.

Les calculs ont été faits par résolution graphique, le procédé est très pratique pour obtenir le résultat d'analyses par étalonnage double. On effectue le tracé de la manière suivante: on porte en ordonnée positive les augmentations de hauteur de saut dues à l'introduction des témoins et en ordonnée négative le saut dû au produit seul. On porte ensuite en abscisse positive le poids des témoins. On trace la droite moyenne passant par les deux points témoins et l'origine; l'endroit où elle coupe l'ordonnée du saut du produit pur détermine en abscisse négative la teneur en produit cherché (voir Fig. 1).

Les résultats trouvés concordent bien avec la valeur indiquée par la maison Hoffmann-La Roche.

b. Dosage de la tyrosine. L'application directe de la méthode mise au point pour le dosage de la tyrosine n'a pas donné immédiatement de bons résultats dans le cas qui nous intéresse. Les sauts étaient de mauvaise qualité et les résultats non reproductibles.

Nous nous sommes donc proposés de reconstituer la peptone étudiée à partir des acides aminés qui la constituent.

Nous nous sommes procuré ces amino-acides et les avons étudiés séparément du point de vue de leur comportement vis-à-vis des divers réactifs que nous utilisons au cours de l'analyse.

Nous pouvons constater qu'aucun de ces produits ne se nitre dans les conditions de travail utilisées pour la tyrosine. L'adjonction de quelques cristaux de nitrite de sodium demeure sans effet. La tyrosine se nitre facilement et correctement en présence de tous ces acides aminés et aucun d'entre eux ne subit lui-même de nitration induite.

A la suite de ces essais, nous avons repris l'étude du dosage et il a pu être constaté que l'erreur provenait de l'emploi d'un trop grand excès de mercure.

(Ceci ne s'était pratiquement jamais produit lors des essais de mise au point sur des substances de composition connue. Certaines perturbations occasionnelles, dues probablement à cette cause, avaient été attribuées à des erreurs de manipulation).

En présence d'une quantité d'acétate mercurique trop considérable et de cristaux de nitrite de sodium, la tyrosine forme une combinaison (de teinte légèrement rougeâtre) qui n'est plus entièrement détruite pendant les deux heures de traitement par l'acide nitrique bouillant.

Pour être dans les meilleures conditions possibles, nous avons modifié un point de la méthode de la manière suivante:

a. On précipite le tryptophane en milieu acide nitrique 0.15 *N* de la manière habituelle. La précipitation étant une réaction lente, il faut que les ions Hg^{+2} restent en solution durant ce temps;

b. Au lieu de procéder ensuite directement à la nitration à partir de cette solution, nous neutralisons par l'hydroxyde de potassium à 20% de manière à éliminer l'excès de mercure sous forme de HgO que l'on centrifuge. On ramène ensuite à la normalité de 0.15 au moyen d'une quantité calculée d'acide nitrique 1 *N*. On ajoute alors seulement le nitrite de sodium et on porte à ébullition à reflux durant 2 h.

TABLEAU XI

Peptone (mg)	*Tyrosine témoin (mg)*	*Saut µA*	*Valeur trouvée (mg)*	%
200	—	0.810	4.7	2.35
200	9.5	2.43		
200	—	0.788	4.75	2.38
200	5.7	1.73		
			Valeur indiquée	2.4

Le reste des opérations demeure sans changement.

En procédant de cette manière, nous avons obtenu des sauts parfaitement réguliers et reproductibles. Les résultats ont été enregistrés dans le Tableau XI.

Les résultats trouvés concordent donc sensiblement avec ceux indiqués par la maison Hoffmann-La Roche.

c. Dosage de la phénylalanine. Les résultats que nous avons obtenus sont les suivants:

TABLEAU XII

Peptone (mg)	*Phénylalanine témoin (mg)*	*Saut µA*	*Valeur trouvée (mg)*	*%*
100	—	1.035	4.1	4.1
100	6.5	2.68		
100	9.3	3.45		
100	—	1.057	4.2	4.2
100	4.3	2.14		
100	8.4	3.17		
			Valeur indiquée	10.9

Les chiffres trouvés sont nettement inférieurs à celui qui nous a été donné. Il est possible qu'une partie de l'amino-acide soit encore lié et ne peut, par conséquent, pas être mise en évidence par notre méthode. Afin de vérifier si l'hydrolyse peut être poussée davantage, nous avons traité une prise de peptone par l'hydroxyde de sodium 5 *N* à 120–125° pendant 5 h, selon le procédé indiqué par BLOCK ET BOLLING[2].

Les analyses ont été ensuite refaites et nous trouvons les chiffres suivants:

TABLEAU XIII

Hydrolysat prise (g)	*Teneur en peptone (mg)*	*Phénylalanine ajoutée (mg)*	*Saut µA*	*Valeur trouvée (mg)*	*%*
2.13	100	—	1.24	4.8	4.8
2.13	100	9.0	3.56		
2.13	100	—	1.26	4.85	4.85
2.13	100	9.2	3.65		

Les résultats sont plus élevés que ceux enregistrés précédemment, il y a donc eu libération supplémentaire de phénylalanine. Mais des hydrolyses plus poussées nous donnent ensuite des valeurs pratiquement constantes allant de 4.8 à 4.9%, il faut donc admettre que la phénylalanine a été entièrement libérée.

La maison Hoffmann-La Roche ne pouvant garantir le chiffre qu'elle nous indique, la constance de nos résultats nous permet de croire qu'ils sont voisins de la teneur réelle en phénylalanine.

En résumé:

Acide aminé	*Valeur indiquée par Hoffmann-La Roche*	*Valeur obtenue*
Tryptophane	2.1	2.02–2.05
Tyrosine	2.4	2.35–2.38
Phénylalanine	10.9	4.80–4.85

Selon les constatations faites au cours des essais de mise au point, la précision des chiffres indiqués est de l'ordre de ±5% environ.

RÉSUMÉ

Il est proposé une méthode polarographique de dosage de la tyrosine, du tryptophane et de la phénylalanine en présence les uns des autres. La méthode est spécifique car les autres acides aminés ne gênent pas la détermination ainsi qu'en témoigne le dosage de la peptone Hoffmann-La Roche. La méthode consiste à nitrer les acides aminés, puis à polarographier le dérivé obtenu. La méthode est sensible et précise car les sauts sont parfaitement bien dessinés. En jouant sur la concentration de l'acide, sur la stabilité différente de ces substances vis-à-vis de l'oxydation et sur la formation de précipité en présence de mercure, il est possible de doser chacun de ces acides aminés en présence des deux autres.

SUMMARY

A polarographic method is described for the determination of tyrosine, tryptophan and phenylalanine in mixtures, in which the animo acids are first converted to their nitro derivatives. Under suitable conditions each of these animo acids can be determined in the presence of the others.

ZUSAMMENFASSUNG

Es wird eine polarographische Methode beschrieben zur Bestimmung von Tyrosin, Tryptophan und Phenylalanin in deren Gemisch. Zur Messung werden die Nitroderivate verwendet. Durch Einhaltung bestimmter Bedingungen können die einzelnen Aminosäuren in Gegenwart der anderen bestimmt werden.

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GRAVIMETRIC DETERMINATION OF ALUMINIUM IN BRONZES AND BRASSES

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The preparation and properties of thioglycolic acid have long been known[1], but significant analytical applications of this acid have been made only recently; an example is the photometric determination of iron[2].

With the ions of some metals, *e.g.* Cu, Ag, Au, thioglycolic acid forms salts which are insoluble in water and in dilute mineral acids[3]; with many other metal ions it possesses a reducing and complexing action which masks the ion. In the latter case, thioglycolic acid is often used along with ammonium benzoate which was introduced by KOLTHOFF *et al.*[4] for the gravimetric determination of aluminium. Its main advantages are that it gives a precipitate, consisting of a mixture of aluminium benzoate and hydroxide, which can easily be filtered and washed; moreover, it prevents almost completely the co-precipitation of the metals of group IV. Precipitation is carried out at pH 3–4. Under the conditions of precipitation of aluminium, Fe^{+3}, Cr^{+3}, Sn^{+4}, Bi^{+3}, Ce^{+4}, Ti^{+4}, Zr^{+4} and Th^{+4} also precipitate[5]. In the presence of thioglycolic acid, which reduces some ions and complexes others, only Al^{+3}, Ti^{+4}, Zr^{+4}, Th^{+4} precipitate[5].

The separation of aluminium with ammonium benzoate has been applied to copper[6] and magnesium[7] base alloys. In both cases the aluminium is subsequently determined as 8-hydroxyquinolate. For copper alloys a sample containing about 10 mg of aluminium is taken; separation of tin and antimony and reduction of the copper with hydroxylamine at pH = 4.2 must be done before the precipitation with benzoate.

Reactions of thioglycolic acid with copper

Thioglycolic acid forms a precipitate with copper, and we have examined the possibility of carrying out a preliminary separation of copper before precipitating aluminium with ammonium benzoate. BERG AND ROEBLING[3] report that thioglycolic acid in acidic solution forms a precipitate with copper; the colour changes from black-blue to pure yellow and one part of the precipitate is soluble in 2 million parts of 0.2 *N* mineral acid solution.

We first prepared two copper precipitates with thioglycolic acid by two different methods.

a. A solution of metallic copper in about 0.4 *N* hydrochloric acid (obtained by adding hydrogen peroxide, which was subsequently destroyed by boiling) was treated with a large excess of thioglycolic acid solution; a whitish precipitate was formed.

b. One volume of 1 *M* copper sulfate solution in about 0.4 *N* hydrochloric acid was treated with two volumes of 1 *M* thioglycolic acid solution; a yellow-whitish precipitate was formed.

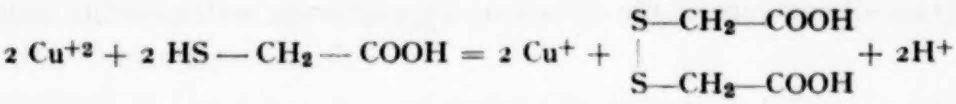
The precipitates were filtered, washed with water, vacuum-dried at 50° and submitted to elemental analysis. The results were:

Method	*Cu* %	*S* %	*C* %	*H* %
a.	41.01	20.66	15.40	2.01
b.	40.98	20.68	15.45	1.98

Evidently the two precipitates are identical and consist of cuprous thioglycolate ($CuSCH_2COOH$). Similar salts of thioglycolic acid with Ba, As, Sb and Pt have been described by KLASON AND CARLSON[8].

When 1 volume of 1 *M* cupric sulfate or nitrate solution in about 0.4 *N* hydrochloric acid is mixed with 1 volume of 1 *M* thioglycolic acid solution, the solution is discolored, *i.e.* copper is reduced, but no precipitate is obtained; on adding another volume of 1 *M* thioglycolic acid solution, cuprous thioglycolate is formed.

When equal volumes of 1 M cuprous chloride solution in about 0.4 N hydrochloric acid and 1 M thioglycolic acid solution are mixed, a precipitate is immediately formed; elemental analysis indicates that it is cuprous thioglycolate. Therefore, in hydrochloric acid solution the copper is first reduced and dithiodiglycolic acid is formed:



$$2\,\mathrm{Cu}^{+2} + 2\,\mathrm{HS-CH_2-COOH} = 2\,\mathrm{Cu}^{+} + \begin{array}{l}\mathrm{S-CH_2-COOH}\\ |\\ \mathrm{S-CH_2-COOH}\end{array} + 2\mathrm{H}^{+}$$

Subsequently, cuprous thioglycolate precipitates:

$$2\,\mathrm{Cu}^{+} + 2\mathrm{HS-CH_2-COOH} = 2\,\mathrm{CuS-CH_2-COOH} + 2\mathrm{H}^{+}$$

If the 1 M cupric sulfate or nitrate solution is prepared in dilute sulphuric or nitric acid rather than in dilute hydrochloric acid, and an equal volume of 1 M thioglycolic acid solution is added, cuprous thioglycolate is immediately formed but copper is still present in the filtrate. This copper is completely precipitated by adding another volume of the thioglycolic acid solution. This difference may be explained by the fact that in hydrochloric solution copper forms the chloro-cuprous ion, $\mathrm{CuCl_3}^{-2}$; therefore, it may be assumed that the cupric ion is first reduced to chloro-cuprous ion and then precipitated by the thioglycolic acid. However, in sulphuric or nitric solution, as soon as the Cu^{+2} ion is reduced to Cu^{+} ion, the latter precipitates as cuprous thioglycolate and some unreduced or unprecipitated copper remains if the amount of thioglycolic acid is inadequate.

With aqueous solutions of cupric sulfate or nitrate in the absence of mineral acids, the thioglycolic acid forms a precipitate which changes from black-blue to yellow. This last precipitate also proved to be cuprous thioglycolate on elemental analysis.

Copper separation and aluminium precipitation

The preliminary separation of copper as cuprous thioglycolate in alloys where it is the base metal is not easy by filtration because the precipitate is very bulky. It is preferable to bring to volume and then filter a portion of the solution before the precipitation of aluminium. In analyses which do not require extreme accuracy, a single precipitation with benzoate is sufficient. When accurate results are desired, double precipitation is essential. With a single precipitation, small amounts of the other elements present in the alloy remain occluded.

The solution may contain up to 0.10–0.12 g of aluminium, but an amount of less than 0.05 g is preferable; its volume must not exceed 100 ml if the aluminium content is less than 10 mg, or 150 ml in other cases. The precipitate must be filtered and washed when warm, otherwise some ammonium benzoate crystallizes in the funnel spout. On cooling, the filtrate becomes cloudy owing to ammonium benzoate, but this dissolves on heating. If it does not, some precipitate has passed into the filtrate. For the double precipitation, the first precipitate can be redissolved on the filter with dilute hydrochloric acid, or the filter may be destroyed by wet combustion. The second method is preferred in order to ensure that all the precipitated aluminium is dissolved; furthermore, if perchloric acid is used, any silica from the beakers or possibly present in the sample can be separated by filtering.

The determination of the aluminium as oxide[9] requires ignition in a platinum crucible and up to 1200° in order to obtain a non-hygroscopic oxide; otherwise, high results are obtained.

The precipitation of aluminium can be carried out also on the nitric acid solution of the alloy from which copper has been removed by electrolysis. However, if the separation of copper is not complete, which may happen if the rectified current is not well-filtered the aluminium oxide obtained by calcining has a feeble blue instead of white color.

EXPERIMENTAL

Reagents (*Merck, pro analysi*)

Dilute hydrochloric acid (1+1), concentrated sulphuric acid, $d = 1.83$, concentrated nitric acid, $d = 1.38$, concentrated ammonia, $d = 0.88$, dilute ammonia (1+1), perchloric acid (60% solution), hydrogen peroxide (30% solution), thioglycolic acid (80% solution).

Ammonium benzoate solution: dissolve 100 g of ammonium benzoate in 700 ml of hot distilled water and dilute to 1000 ml with distilled water (if the benzoate precipitates when the solution is cold, heat before use).

Benzoate wash solution: dissolve 10 g of ammonium benzoate in 800 ml of distilled water, add 20 ml of glacial acetic acid and dilute to 1000 ml with distilled water.

Bromophenol blue indicator: triturate 0.40 g of bromophenol blue with 8.5 ml of 0.1 *N* NaOH; dilute to 100 ml with distilled water.

PROCEDURE

In a 500-ml flask, dissolve 1 or 2 g of alloy (depending on whether aluminium is more or less than 5%) with 40 ml of 1:1 hydrochloric acid and add slowly 30% hydrogen peroxide solution. When the alloy does not respond to hydrogen peroxide, *e.g.* manganese bronzes, use dilute nitric acid instead of hydrogen peroxide. To complete the dissolution of metal heat moderately, dilute with 150 ml of distilled water and boil for about 10 min to remove hydrogen peroxide.

At 60°–80° add gradually while stirring, 20 ml of 80% thioglycolic acid solution, cool under the tap and bring to volume with distilled water. Through a dry Whatman No. 40 paper, filter 250 ml of the solution into a graduated flask. Transfer the contents into a tall-form 400-ml beaker, washing the flask with distilled water. Concentrate to 100 or 150 ml depending on whether the aluminium content is more or less than 10 mg. At 70° add 20 ml of the ammonium benzoate solution and stir with a glass rod to dissolve any precipitate formed. Add a few drops of bromophenol blue indicator and then dilute 1:1 ammonia until the indicator starts to change color. The solution must have a pH of 3.5 to 4 which may be checked by narrow-range pH paper. Boil for 5 min while stirring. Allow to settle for a few minutes and filter on a Whatman No. 40 paper, washing at least three times with the hot benzoate wash solution. Transfer the filter and precipitate back to the original beaker, add 10 ml of sulfuric acid ($d = 1.83$), let the paper carbonize, add 15 ml of nitric acid ($d = 1.38$), cover with a watchglass and heat moderately until all nitrous vapors are removed.

Then wash the watchglass and beaker walls carefully with distilled water. Remove the watch glass and heat to fumes of sulphuric acid. Remove the beaker from the plate, add immediately 5 ml of 60% perchloric acid and then reheat to fumes of perchloric acid.

As the perchloric acid fumes thicken, the residual organic substances are destroyed and the solution becomes colorless.

Allow to cool and dilute with distilled water to about 80 ml rinsing the glass walls; boil for a few minutes, allow to cool down to below 50°, and filter on Whatman No. 40 paper into a tall-form 400-ml neutral glass beaker washing with distilled water. This filtration may be omitted if the solution is perfectly clear, but it is generally advisable because some silica, though almost invisible, is always present.

Concentrate the filtrate to less than 100 ml, if the aluminium present is less than 10 mg; then, at about 70°, add 2 ml of the thioglycolic acid solution and re-precipitate the aluminium with ammonium benzoate as described above.

Filter on Whatman No. 40 paper and wash several times with hot benzoate wash solution. Place the filter and the precipitate in a weighed platinum crucible, dry and burn the filter, calcine in a muffle at 1200° for 2 h, cool in a desiccator and weigh.

$$\text{Al}\ \% = \frac{\text{weight of Al}_2\text{O}_3 \times 52.91}{\text{sample weight}}$$

RESULTS

The method described has been used to determine aluminium in synthetic solutions and in N.B.S. standards. The synthetic solutions were prepared from suitable weighed amounts of metallic copper and aluminium, to which were added convenient aliquots of solutions of known composition containing the other elements. These solutions were obtained by dissolving the metal concerned in dilute hydrochloric acid and a little dilute nitric acid.

The composition of the synthetic solutions was varied to simulate determinations on different percentages of aluminium (from 0.5% to 10%) and in the presence of different amounts of the elements generally found in copper alloys.

The results obtained (Tables I, II and III) are mostly satisfactory; the highest probability of errors appears when the aluminium content is high (about 10%) and low results are obtained. It is therefore advisable to use samples that contain less than about 0.05 g of aluminium. Table IV shows the results obtained by a single precipitation of the aluminium. The values found are rather high; the spectrographic examination indicates that the aluminium precipitate is contaminated by small amounts of the other alloying elements. Hence a double precipitation is necessary to ensure pure precipitates.

Table V shows the results obtained with some N.B.S. standards. Some of these samples lacked aluminium which was then added in varying percentages. On standard 164, determinations were made on both 1-g and 2-g samples; the results obtained agree in all cases with the certified values.

ACKNOWLEDGEMENTS

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TABLE I

DETERMINATIONS ON SYNTHETIC SOLUTIONS

No.	*Weight (g)*		*Al %*	
	Cu	*Al*	*calculated*	*found*
1	1.9820	0.0258	1.28	1.28
2	1.9798	0.0228	1.13	1.16
3	1.9200	0.0844	4.21	4.25
4	1.8416	0.1614	8.05	8.06
5	1.8404	0.1650	8.22	8.24
6	1.8012	0.2070	10.31	10.28
7	1.8022	0.2058	10.25	10.29
8	1.8000	0.2020	10.09	10.09
9	1.9990	0.0072	0.31	0.34
10	2.0008	0.0068	0.30	0.29
11	1.9908	0.0122	0.54	0.59
12	1.9812	0.0248	1.09	1.12
13	1.9816	0.0212	0.93	0.96

continued

TABLE I (continued)

No.	*Weight (g)*		*Al %*	
	Cu	*Al*	*calculated*	*found*
14	1.9216	0.0870	3.84	3.87
15	1.9226	0.0855	3.77	3.78
16	1.9218	0.1606	6.87	6.86
17	1.9216	0.1684	7.18	7.15
18	1.7618	0.2446	10.81	10.79
19	1.7620	0.2438	10.79	10.78
20	1.7656	0.2470	10.85	10.62
21	1.7606	0.2396	10.60	10.51
22	1.7623	0.2380	10.53	10.28
23	1.7638	0.2450	10.78	10.78
24	1.7660	0.2461	10.82	10.71
25	1.7648	0.2412	10.65	10.53

Other elements present (g)

		Fe	Mn	Ni	Zn	Pb
Tests	1–8	—	—	—	—	—
Tests	9–25	0.05	0.05	0.05	0.10	0.005

TABLE II

DETERMINATIONS ON SYNTHETIC SOLUTIONS

No.	*Weight (g)*		*Al %*	
	Cu	*Al*	*calculated*	*found*
1	1.7600	0.0977	4.32	4.37
2	1.7600	0.0955	4.29	4.27
3	1.7600	0.1107	4.91	4.90
4	1.7600	0.1252	5.48	5.50
5	1.7600	0.1031	4.58	4.58
6	1.7600	0.1032	4.58	4.58
7	1.7600	0.1015	4.51	4.52
8	1.7600	0.1073	4.75	4.73
9	1.9220	0.0840	3.67	3.68
10	1.9217	0.0818	3.58	3.56
11	1.8405	0.1668	7.29	7.32
12	1.9612	0.0433	1.97	2.00
13	2.0002	0.2495	9.75	9.73
14	1.7597	0.2448	10.62	10.58
15	1.7613	0.2514	10.82	10.78
16	1.7600	0.2460	10.62	10.61
17	1.7600	0.2433	10.65	10.56
18	1.7600	0.2432	10.65	10.57
19	1.7600	0.2461	10.76	10.67
20	1.7600	0.2403	10.53	10.56

Other elements present (g)

		Fe	Mn	Ni	Zn	Pb
Tests	1–4	0.05	0.05	0.05	0.10	0.006
Tests	5–8	0.05	0.05	0.05	0.10	0.012
Tests	9–20	0.05	0.05	0.05	0.10	0.030

TABLE III

DETERMINATIONS ON SYNTHETIC SOLUTIONS

No.	*Weight (g)*		*Al %*	
	Cu	*Al*	*calculated*	*found*
1	1.9230	0.0860	4.15	4.16
2	1.9212	0.0872	4.21	4.24
3	1.8412	0.1633	7.90	7.88
4	1.8436	0.1656	7.99	8.04
5	1.7390	0.2639	12.79	12.66
6	1.7426	0.2670	12.89	12.83
7	1.9936	0.0100	0.42	0.46
8	1.9936	0.0108	0.45	0.48
9	1.9932	0.0140	0.58	0.61
10	1.9808	0.0204	0.84	0.88
11	1.9816	0.0221	0.93	0.94
12	1.9798	0.0226	0.95	0.95
13	1.9224	0.0852	3.57	3.53
14	1.9036	0.1041	4.37	4.34
15	1.9046	0.1070	4.49	4.42
16	1.8634	0.1410	5.93	5.89
17	1.8602	0.1454	6.12	6.18
18	1.8420	0.1666	10.00	10.10
19	1.7420	0.2649	11.14	11.14

Other elements present (g)

		Fe	Mn	Ni	Zn	Pb	Sn
Tests	1-6	—	—	—	—	—	0.06
Tests	7-9	0.05	0.05	0.05	0.10	0.06	0.06

TABLE IV

RESULTS OBTAINED BY A SINGLE PRECIPITATION OF ALUMINIUM

No.	*Weight (g)*		*Al %*	
	Cu	*Al*	*calculated*	*found*
1	1.7604	0.2402	10.61	10.71
2	1.7614	0.2454	10.81	10.99
3	1.7622	0.2398	10.59	10.73
4	1.7676	0.2517	11.03	11.11

Other elements present (g)

		Fe	Mn	Ni	Zn	Pb
Tests	1-4	0.05	0.05	0.05	0.10	0.0125

TABLE V

DETERMINATIONS ON N.B.S. STANDARDS

Composition	*Weighed sample g*	*Al added g*	*Al %*	
			calculated	*found*
N. 63c Phosphor bronze	1.9905	0.0132	0.65	0.64
	1.9925	0.0186	0.92	0.93
Cu = 80.46 Sb = 0.52	1.9821	0.0235	1.17	1.17
Pb = 9.35 Ni = 0.32 S = 0.06	1.9032	0.1025	5.11	5.13
Sn = 9.03 P = 0.15 As = 0.02	1.9027	0.1053	5.24	5.30
Fe = 0.002 Zn = 0.09				

continued

TABLE V (continued)

Composition	*Weighe sampled* *g*	*Al added* *g*	*Al %* *calculated*	*Al %* *found*
N. 52c Cast bronze	1.9895	0.0127	0.63	0.66
	1.9914	0.0169	0.84	0.86
Cu = 89.25 Ni = 0.76 P = <0.001	1.9831	0.0208	1.03	1.06
Sn = 7.85 Pb = 0.011 S = 0.002	1.9824	0.0220	1.09	1.08
Zn = 2.12 Fe = 0.004	1.9006	0.1040	5.19	5.22
	1.9010	0.1054	5.25	5.28
N. 164 Al–Mn bronze	2	—	6.21	6.18
	2	—	6.21	6.17
	2	—	6.21	6.16
Cu = 63.76 Sn = 0.63	2	—	6.21	6.19
Zn = 21.89 Pb = 0.22	2	—	6.21	6.17
Mn = 4.68 Ni = 0.046	2	—	6.21	6.19
Fe = 2.52 Si = 0.038	2	—	6.21	6.16
Al = 6.21	1	—	6.21	6.22
	1	—	6.21	6.25
	1	—	6.21	6.18
	1	—	6.21	6.21
N. 62c Manganese bronze	2	—	1.22	1.20
	2	—	1.22	1.25
Cu = 59.16 Fe = 0.74 Ni = 0.28	2	—	1.22	1.20
Zn = 37.24 Mn = 0.66 Pb = 0.24	2	—	1.22	1.21
Al = 1.22 Sn = 0.39 Si = 0.068	2	—	1.22	1.22
N. 158 Silicon bronze				
	2	—	0.54	0.52
Cu = 90.86 Fe = 1.48 *Al = 0.54*	2	—	0.54	0.52
Si = 2.72 Mn = 1.31 Ni = 0.006	2	—	0.54	0.53
Zn = 2.07 Sn = 0.97 Pb = 0.004	2	—	0.54	0.52

SUMMARY

The gravimetric determination of aluminium in bronzes and brasses is described. After separation of copper by thioglycolic acid, aluminium is determined with ammonium benzoate.

RÉSUMÉ

Une méthode est proposée pour le dosage gravimétrique de l'aluminium dans des bronzes et des laitons. On procède par précipitation de l'aluminium au moyen de benzoate d'ammonium, après séparation du cuivre par l'acide thioglycolique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur gravimetrischen Bestimmung von Aluminium in Bronzen und Messing. Kupfer wird mit Thioglycolsäure abgetrennt und das Aluminium mit Ammoniumbenzoat gefällt.

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A SIMPLE SATURATED CALOMEL REFERENCE ELECTRODE FOR POLAROGRAPHY

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INTRODUCTION

All reference electrodes[1,2] used in polarography are sensitive to movement except the Ladisch and Knesbach[3] design; in general their construction requires a platinum to glass seal, or glass blowing experience. The half-cells described in the present paper have the following advantages. Their shape permits maximum interphase contact with a minimum amount of reagents in an electrode body that fits into an H-cell; this contributes to the more efficient use of the latter. They have a low

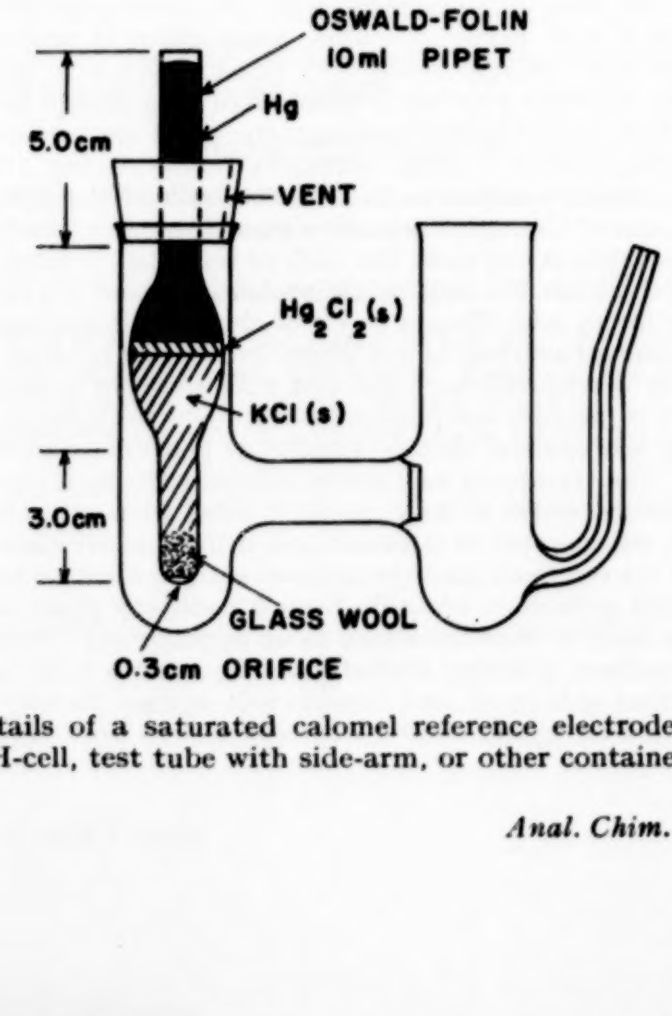

Fig. 1. Construction details of a saturated calomel reference electrode body that fits into an H-cell, test tube with side-arm, or other container.

resistance and the resulting saturated calomel electrodes can be transported without alteration of their 'potential' characteristics.

METHOD

The simplest fabrication technique is to cut a 10-ml Oswald-Folin pipet to the dimensions indicated in Fig. 1 and fire-polish the delivery end until an orifice of approximately 0.3 cm is formed to hold a glass wool plug; the resulting half-cell has a slightly higher resistance than one with a sintered glass tip. The sintered glass tip, which is an alternative choice, is made by sealing the delivery tip and filling it to a depth of approximately 3 cm with 60–80 mesh ground glass obtained by pounding, rather than grinding, the sections cut from the pipets. The body is evacuated (and kept under vacuum) while the tip is slowly heated and rotated in the upper part of a Meker burner flame until the extreme end fuses and more than half of the inner wall area of the tip appears frosted.

The vacuum line is disconnected when the tip has cooled just sufficiently to permit handling, and any excess unsintered glass is removed. With a thin file, such as is used to open ampoules, the tip is deeply scored completely around at the point where the break is to be made so as to form a 0.5-cm sintered glass plug.

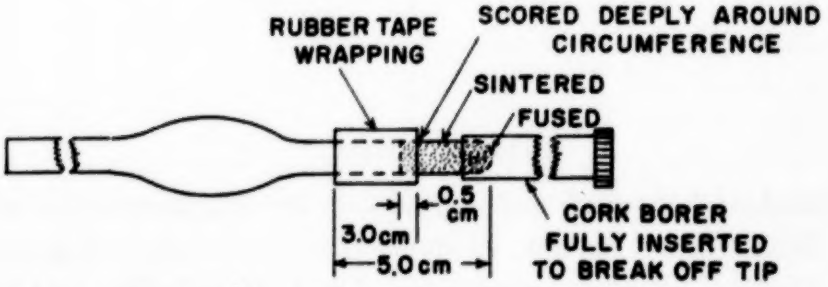
RUBBER TAPE WRAPPING
SCORED DEEPLY AROUND CIRCUMFERENCE
SINTERED
FUSED
0.5 cm
3.0cm
5.0 cm
CORK BORER FULLY INSERTED TO BREAK OFF TIP

Fig. 2. Mode of breaking off fused glass extremity of pipet without shattering the sintered glass tip.

To protect the latter from shattering, a 10-cm, length of rubber tape is wrapped round the tip so that the lower edge of the wrapping coincides with the scoring in the glass tubing (Fig. 2). The rubber covered tubing is held firmly (avoiding application of pressure to the bulb) while inserting the fused glass end into a snugly fitting cork borer which acts as a lever in effecting the break. The suitability of the sintered glass tip or glass wool plug should be checked by filling the pipet with distilled water and observing the drainage; the pipet should be empty in 35 to 50 sec.

The resulting body is immersed in a large vertically mounted test tube containing enough saturated C.P. potassium chloride solution to half-fill the bulb of the pipet. Finely ground solid potassium chloride is introduced through a stemless glass funnel in small portions (with simultaneous rotation to avoid stratification) until the bulb of the pipet is filled to the half-way mark.

The saturated liquid level within the bulb is maintained at least 0.5 cm above the solid, and the salt is allowed to settle for 15 min. Then 3 to 5 g of electrolytic mercurous chloride are added in small amounts with occasional swirling of the pipet, to wet the calomel. After standing undisturbed for 30 min, the body is removed from the test tube to allow complete drainage of excess solution. A few small drops of mercury are poured gently down the sides of the tube into the bulb (without directly touching the calomel surface insofar as possible) and the pipet is rotated to cause packing of the salts. The remaining free space is filled with mercury and the body is reimmersed in an H-cell or test tube which is three-quarters filled with saturated potassium chloride.

Twenty-four hours later, the mercury is removed and if there is evidence of channeling or large drops are embedded, these are removed, and the calomel surface must be reconditioned by adding a small amount of saturated potassium chloride from a capillary pipet, swirling, draining, and refilling with mercury. The body is then immersed in an appropriate container, such as an H-cell (Sargent #S-29400 with medium porosity fritted glass disc and 4.5-cm agar plug) or test tube with side-arm (A. H. Thomas #6243-A) and flexible salt bridge. In any case, the stopper and inside lip of the vessel should be lightly coated with vaseline to limit creeping of the potassium chloride.

DISCUSSION

Half-cells which had bodies containing glass wool plugs or sintered glass tips, and were inserted into the arm of an H-cell, had resistances of 540 to 680 ohms (measured by the PESCE, KNESBACH AND LADISCH method)[4]; if the container was a test tube with side-arm and flexible salt bridge, the respective resistances were 890 to 1070 Ω. The bridge had a diameter of 0.5 cm, and was 36.2 cm long of which 15 cm was an 0.8-cm outside diameter gas washing tube filled to a depth of 13.7 cm with agar–potassium chloride. The coarse 1.7-cm fritted glass tip was kept in saturated potassium chloride when not in use.

The resistances of the suggested half-cell designs compared favorably with that of the large-area saturated calomel electrode, prepared in a Heyrovsky vessel with a side-arm bent to 180° and connected to the same salt bridge, which had an impedance of 720 Ω. The reproducibility of replicate limiting current measurements, regardless of the type of reference half-cell used, did not vary by more than 1.0%. The average potential of these electrodes *versus* a quinhydrone half-cell was 0.228_0 V with extreme values of 0.227_4 and 0.229_0, and a standard deviation of 0.000_6, as compared to 0.227_4, 0.228_2, and 0.228_9 for the large area saturated calomel electrode.

Saturated calomel electrodes, prepared by the method indicated above, have been used continually for the past two years in the Occupational Health laboratories of Bolivia, Colombia and Perú because it is considerably easier to change the solution to be analyzed and rinse the other arm of the H-cell. These half-cells have maintained their characteristics and are expected to last indefinitely.

The mode of making the sintered glass tip is described because it is much simpler than previously published information.

SUMMARY

A saturated calomel reference electrode which can be readily assembled is described. This half cell has a low resistance, is easily transportable, and materially increases the efficiency of the H-cell in polarography.

RÉSUMÉ

Une nouvelle électrode de référence au calomel est proposée; elle peut être utilisée en analyse polarographique et elle présente certains avantages.

ZUSAMMENFASSUNG

Es wird eine neuartige Kalomel Bezugselektrode beschrieben, die sich bei der polarographischen Analyse verwenden lässt und gewisse Vorteile besitzt.

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THE SIMULTANEOUS DETERMINATION OF COPPER AND IRON IN HIGH PURITY ALUMINIUM USING THE K 1000 CATHODE RAY POLAROGRAPH

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(Received August 20th, 1959)

A method is described for the rapid simultaneous determination of copper and iron in high purity aluminium (>99.99%). It is based on the solubility of high purity aluminium in sodium hydroxide solutions. It is only required to dissolve a weight of the sample in a 20% solution of sodium hydroxide, to add a solution of sucrose[1] and to analyze polarographically.

A polarographic method for the analysis of high purity aluminium was first carried out by SEMERANO[2] applying preliminary separation of copper, lead, cadmium, nickel, zinc and iron as sulphides and re-dissolving the sulphides in nitric acid. The method is very tedious and requires extremely high analytical skill.

Copper present in aluminium in amounts less than 50 μg is not reduced by hydrogen to the metallic state in the process of dissolving the aluminium in sodium hydroxide. The iron is converted into ferrous hydroxide, which is soluble in sodium hydroxide. This behaviour of copper and iron in connection with the high sensitivity of the Cathode Ray Polarograph[3-5] was the basis for the development of the method.

The present method is very rapid, fully eliminating chemical manipulations, such as filtering, extraction, etc., and enables the simultaneous estimation of copper and iron within 15 to 20 min, with a tolerance of ±0.0001% for copper contents <0.005%, ±0.00001% for iron contents <0.0001% and ±0.0001% for iron contents between 0.0001% and 0.005%.

EXPERIMENTAL

To observe the linearity of the peak heights of copper and iron with the actual concentrations of these metals in aluminium, the following investigations were carried out.

0.1 g of super purity aluminium were introduced into five 5-ml flasks. By means of a precision microburette, 0.01–0.04 ml of standard solutions of copper and iron were added to each flask to increase the concentration by 0, 10, 20, 30 and 40 p.p.m. for copper, and 0, 0.1, 0.2, 0.3 and 0.4 p.p.m. for iron. 1.5 ml of a 20% solution of sodium hydroxide were added to each flask and the samples brought into solution by placing them on a low heated hot plate and carefully controlling the violence of the reaction by lifting the flask when necessary. When the samples were completely dissolved, the flasks were cooled, 0.5 ml of M sucrose were added, and the solutions made up to the mark with water. This technique was used due to small quantity of super purity aluminium available at the time. By having larger samples (0.5 to 1 g), placing them in 50-ml tall pyrex beakers covered by watch glasses, and adding a corresponding volume of sodium hydroxide, the process of dissolving the aluminium is simplified by placing the beaker on a hot plate, and if the reaction becomes too violent, arresting it by injecting water from a wash bottle. After cooling, the solutions are transferred into 10–20 ml flasks, sucrose added in the rate stated above, and made up to the mark with water. The polarograms are recorded on 5 ml of the solutions after deaerating with nitrogen for 3 min. In the experiment, the polarograms were recorded on start potential —0.1 V for copper, scale factor 0.04 and start potential —0.6 V for iron, scale factor 0.06. The concentrations of each element and corresponding peak heights are tabulated below.

TABLE I

Sample	*Copper added p.p.m.*	*Peak height divisions*	*Iron added p.p.m.*	*Peak height divisions*
1	0	0	0	16
2	10	10	0.1	20
3	20	21	0.2	24
4	30	30	0.3	27
5	40	40	0.4	31

No copper was detected in the original sample. Iron was present in the sample and the concentration is easily calculated. As the addition of 0.1 p.p.m. has an increase in wave-height of 4 divisions, the peak height (16 divisions) on the original sample corresponds to 0.4 p.p.m. The polarogram on 5 ml of the blank showed no presence of iron. Typical polarograms of copper and iron are shown below (Figs. 1 and 2).

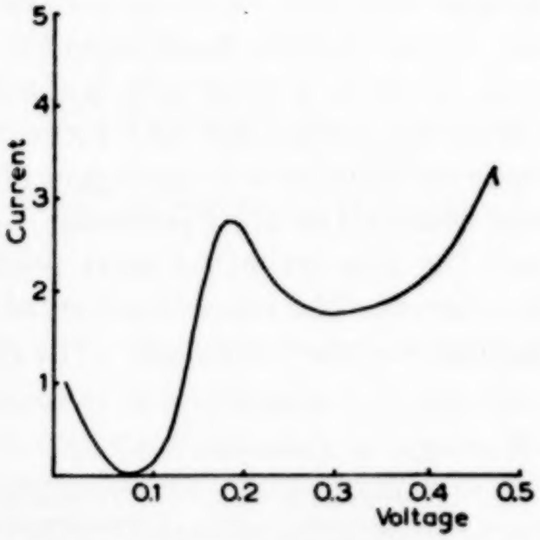

Fig. 1. Typical reduction wave of copper in aluminium.

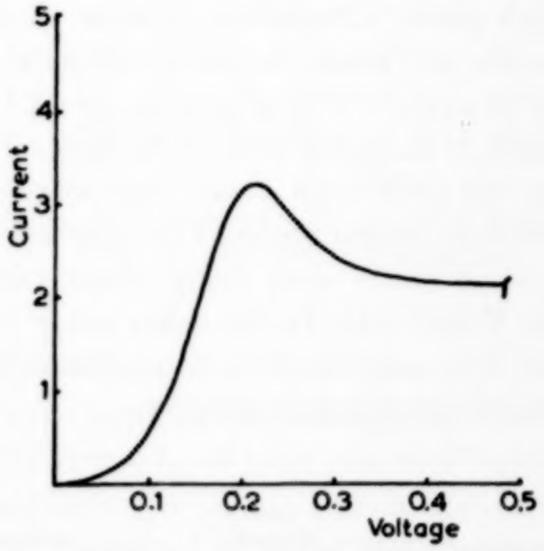

Fig. 2. Typical reduction wave of iron in aluminium.

During the investigation, the effect of the presence of lead on the reduction waves of copper and iron was studied, and also the effect of the addition of various concentrations of EDTA to the basic electrolyte. The addition of lead in various concentrations showed no interference with either the copper or iron peak heights. Lead is reduced with the formation of a well shaped wave preceding Fe-wave, hence indicating the possibility of determining all three metals simultaneously (Figs. 3 and 4). The addition of a saturated solution of EDTA from 0.5 to 2% results in no significant alteration in the shape of the waves or in the peak heights. An increase in EDTA to over 3% depresses the copper wave, and increases the height of the iron wave. An addition of 6% EDTA completely removes the copper wave, and increases the peak height for iron by 25%. EDTA must be used in the basic electrolyte when the manganese content is considerably higher than the iron content. Manganese interferes with the determination of iron, but this can be overcome by the addition of 2% of a saturated solution of EDTA, as manganese is not reduced in its presence.

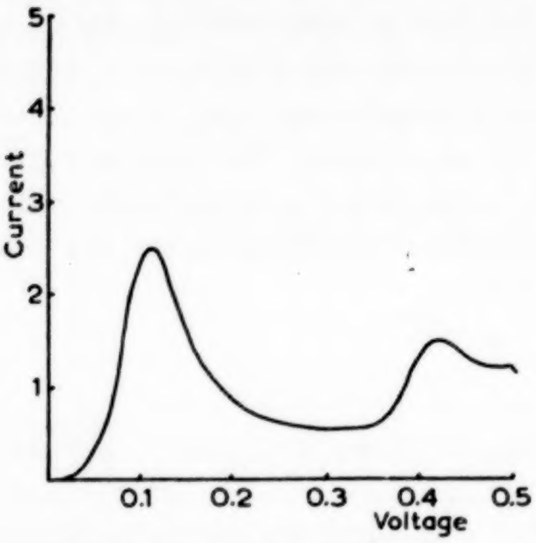

Fig. 3. Simultaneous determination of Cu and Pb in aluminium (20 p.p.m. Cu, 20 p.p.m. Pb).

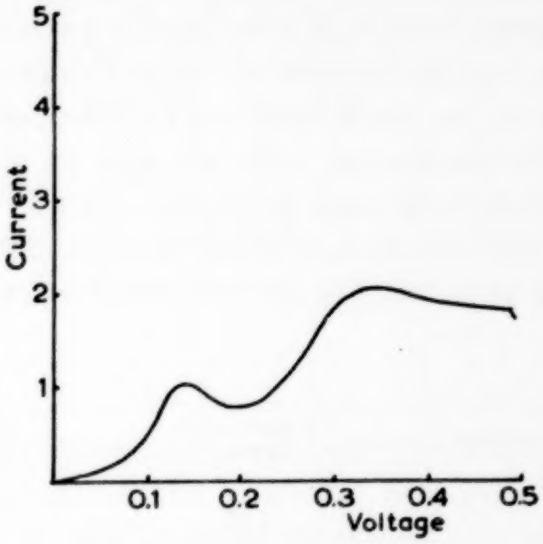

Fig. 4. Simultaneous determination of Pb and Fe in aluminium (20 p.p.m. Pb, 1 p.p.m. Fe).

To show that the method could be applied for the routine control of the analysis of high purity aluminium, a series of seven samples was used, with copper and iron contents previously found by classical methods, by the British Aluminium Co. Ltd. 0.5 g of sample were placed in 50-ml beakers, dissolved in 5 ml of 20% sodium hydroxide, transferred into 10-ml flasks, 2 ml of M sucrose added and the solution made up to the mark with water. The polarograms were recorded on a 5-ml aliquot of each solution as stated above. The copper waves were observed on start potential —0.1 V and scale factor 0.04 using direct current, and the iron waves on start potential —0.6 V and scale factor 0.004 using derivative current. The concentrations of each metal were calculated by comparison, taking sample 3 as the "standard". The results obtained are tabulated below.

TABLE II

Sample	*Cu found by classical method p.p.m.*	*Cu found by polarographical method p.p.m.*	*Fe found by classical method p.p.m.*	*Fe found by polarographical method p.p.m.*
1	5	3	5	8
2	5	3	5	9
3	10	10	5	5
4	10	10	5	9
5	15	18	10	9
6	15	19	20	15
7	35	30	10	10

The copper content of each sample was also estimated by standard addition using a precision microburette and introducing directly into the cell 0.01 ml of a standard copper solution (0.3 mg/ml). Figs. 5 and 6 illustrate the copper wave in sample 1 before and after the addition of 3 µg of copper. Wave height on original sample is 10 divisions and after addition is 45 divisions. Hence 3 µg of copper corresponds to a wave height of 35 divisions, and

$$10 \text{ divs.} = \frac{3}{35} \times 10\ \mu g = 0.86\ \mu g$$

Weight of sample in the cell = 250 mg, thus concentration of copper

$$= \frac{0.86 \times 10^6}{250 \times 10^3} \text{ p.p.m.}$$
$$= 3 \text{ p.p.m.}$$

Standard addition cannot be applied for iron determination due to the slow reaction of iron with sucrose, to form a reducible iron complex. The iron content could be obtained from a calibration graph prepared from high purity aluminium as described above.

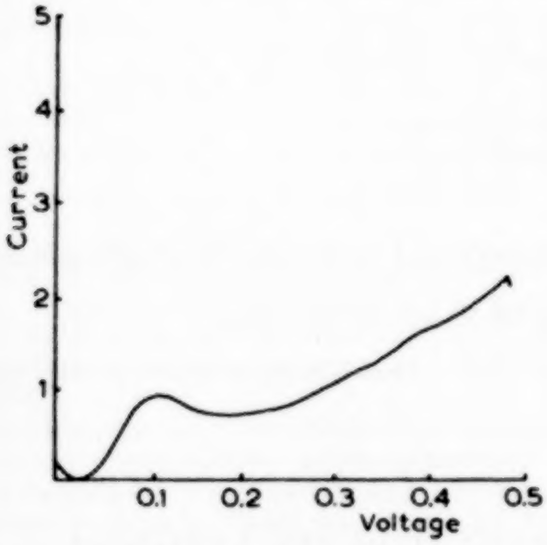

Fig. 5. Reduction wave of copper in sample 1.

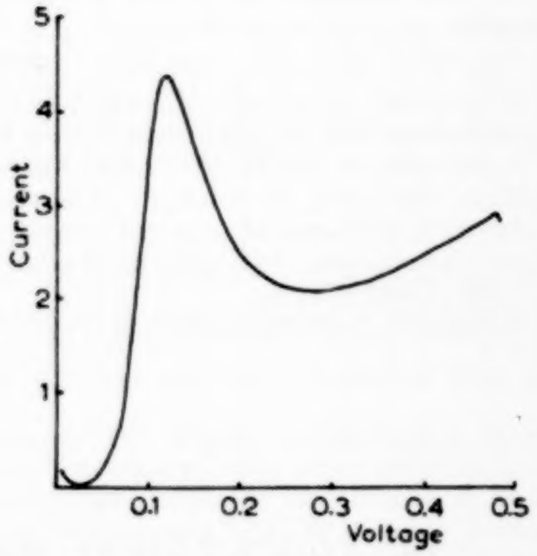

Fig. 6. Reduction wave of copper in sample 1 after the addition of 3 µg of Cu.

DISCUSSION OF RESULTS

The method is applicable only for the analysis of high purity aluminium. Its simplicity, speed and accuracy is demonstrated, and it will be of high practical value in laboratories where a large number of determinations are required. This method could not be used on conventional polarographs as the quantity of the element under consideration is very small (<50 µg). The saving of time and reagents in the analysis is enormous compared with existing chemical[7] or polarographic[2,6,7] methods.

All measurements have been carried out at a temperature of 25°, using a mercury-pool as reference electrode throughout the investigation. All potentials are given on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as ±0.246 V *versus* the normal hydrogen electrode (N.H.E.).

ACKNOWLEDGEMENTS

The author wishes to express his thanks to the Directors of Southern Instruments Limited for permission to publish this work, and to the British Aluminium Company Limited for supplying the necessary samples.

SUMMARY

An accurate simultaneous determination of copper and iron in 99.99% aluminium can be carried out in 10–15 min, using the linear sweep polarograph. Lead can also be determined in the same solution. The basic electrolyte used is sodium hydroxide and sucrose, but the addition of ethylenediaminotetraacetic acid (EDTA) is necessary if manganese is present. The effect of EDTA on the reduction wave of copper and iron has been investigated.

RÉSUMÉ

Une méthode rapide est décrite pour le dosage polarographique du cuivre et du fer dans un aluminium très pur (> 99.99%). Le plomb peut être dosé dans la même solution. En présence de manganèse, l'addition d'acide éthylènediaminotétracétique (EDTA) est nécessaire. L'influence de ce dernier (EDTA) sur la réduction du cuivre et du fer a été examinée.

ZUSAMMENFASSUNG

Es wird eine Schnell-methode beschrieben zur polarographischen Bestimmung von Kupfer und Eisen in Aluminium von 99.99% Reinheit. Blei kann ebenfalls in der gleichen Lösung bestimmt werden. Die Gegenwart von Mangan erfordert einen Zusatz von Aethylendiaminotetraessigsäure (EDTA). Der Einfluss des EDTA Zusatzes auf die Reduktion des Kupfers und Eisens wurde untersucht.

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SPECTROCHEMICAL DETERMINATION OF LITHIUM, SODIUM, POTASSIUM AND RUBIDIUM IN ROCKS AND MINERALS USING THE STALLWOOD JET

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(Received August 29th, 1959)

The Stallwood jet[1] has been used extensively during the last five years at McMaster University for analysis of silicate rocks and minerals. Two methods developed for some major, minor and trace-elements have already been described[2,3], but in neither of these was it feasible to determine the alkali metals, especially lithium and rubidium.

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Anal. Chim. Acta, 22 (1960) 398–400

Experiments were therefore carried out to develop a method suitable for lithium, sodium, potassium and rubidium in their usual concentration ranges. The yellow-infrared spectral region affords the most sensitive lines. Thallium and caesium were tried as internal standards, and the latter was chosen because of more satisfactory lines and sensitivity.

The spectrograph was a Jarrel-Ash Co. 21-foot grating instrument, Wadsworth mount, using the first-order spectrum with dispersion of 5.2 A/mm. The optical train was standard and comprised a spherical lens, a diaphragm of 1-cm aperture serving as a secondary source, and a pair of crossed cylindrical lenses. Further details of the method are given in Table I.

TABLE I

SPECTROCHEMICAL PROCEDURE

Slit	11 mm long; 30 μ wide.
Arc-gap	5 mm
Intensity reduction	Rotating step-sector with log intensity-ratio 0.2 adjacent to the slit.
Filter	Corning Glass Co. No. 3486 (yellow), to absorb UV.
Voltage	230 V on open-circuit.
Current	5 A
Gas-flow	4 l air/min
Exposure	100 sec
Electrodes	Lower (anode), 1/8 inch graphite rod with plain crater 1.5 by 6 mm; upper, 1/8 inch rod: both of National Carbon Co. "Special" Grade.
Emulsion and range	Eastman-Kodak Type I-N, 5750–8250 Å.
Processing	4 min in D-19 developer at 20°, stop-bath, acid fix and wash.
Sample	2 parts mineral, 1 part Cs_2CO_3, 1 part graphite.

Line transmission was measured with an Applied Research Laboratories densitometer and plate calibration curves were constructed in the usual manner. Calculations of the ratio of log intensity analysis line to internal standard line (corrected for background) were made on a calculating-board[4]. Samples were analysed in triplicate, usually with one spectrum on each of three pairs of plates.

Working-curves were established by arcing standards. For lithium and rubidium these were artificial, prepared from Johnson-Matthey "Specpure" chemicals, using a matrix close to granite in composition. For sodium and potassium both artificial standards and National Bureau of Standards clays and feldspars were used. The materials were mixed by hand in agate mortars and some trouble was experienced with the caesium carbonate, which is hygroscopic and must be weighed and mixed as soon as possible after removing it from the dessicator, in which it should be stored.

TABLE II

SPECTRAL LINES AND PRECISION DATA

Element	*A*	*E* %	*Determined*		*Recommended*	
			G-1	*W-1*	*G-1*	*W-1*
Li	6707.844	5.1	26 p.p.m.	12 p.p.m.	21 p.p.m.	13 p.p.m.
Li	6103.642					
Na	8183.270					
Na	6160.760	9.1	3.27%		3.25%	
K	7698.979					
K	6938.980	4.6	7.4 %		5.42%	
Rb	7800.227	5.2	283 p.p.m.	24 p.p.m.	214–254 p.p.m.	21–29 p.p.m.
Cs	6983.488		Internal standard			

Spectral lines are listed in Table II. All are free of line interference of the kind expected in normal silicate minerals, but Li 6103 and Na 6160 have troublesome interference from a calcium oxide band spectrum in Ca-rich samples such as W-1. The Cs line is rather diffuse but can be measured satisfactorily over a wide range of transmission values. K 7698 shows self-absorption at concentrations above 0.4% K_2O and K 6938 could only be measured down to 1.7%: samples falling within the gap must be diluted and measured on K 7698, or must have potassium added so that they can be measured on K 6938. Wherever possible the standard rocks G-1 and W-1 were analysed (usually 12 times) and the results are included in Table II, along with representative values from the literature: the latter include lithium and rubidium[5], and sodium and potassium[6].

The working-curves were computed statistically following a method which has been described elsewhere[7]. This procedure also gives a value for the standard deviation for triplicate analysis, which is divided by the amount present and converted to per cent to obtain the relative error *E*, also given in Table II. *E* was not evaluated for several of the lines used, because few of the samples to be analysed fell in the ranges in which they could be used, but by visual inspection appears to be from 5-10%.

The analyses of G-1 and W-1 are satisfactory except for Rb in G-1, which is somewhat high, and for K 6938 which gave the high value of 7.4 % K_2O for G-1. The disagreement is serious and the working-curve for K 6938 needs re-calibration.

Owing to the one hundred per cent dilution of the sample and the buffering action of both diluents, combined with the features of the STALLWOOD jet, matrix effects are at a minimum and the method appears suitable for a wide variety of silicates.

ACKNOWLEDGEMENTS

The authors wish to acknowledge financial assistance from the National Research Council of Canada and the Geological Survey of Canada.

SUMMARY

A D.C. spectrochemical method using the STALLWOOD jet has been developed for the determination of Li, Na, K and Rb in silicate minerals and rocks. Samples are mixed with graphite and Cs_2CO_3 in the ratio 2 : 1 : 1, and Cs serves as internal standard. Precision and accuracy is satisfactory.

RÉSUMÉ

Une méthode spectrochimique est proposée pour le dosage de Li, Na, K et Rb dans des minéraux et des roches silicatées. On mélange les échantillons à analyser, en poudre, avec du graphite et du carbonate de césium (Cs étant utilisé comme étalon interne).

ZUSAMMENFASSUNG

Es wird eine spektrochemische Methode beschrieben zur Bestimmung von Li, Na, K und Rb in Mineralien und Silikatgesteinen, unter Verwendung des ,,STALLWOOD jet''. Die zu analysierende Substanz wird mit Graphit und Cäsiumcarbonat vermischt, wobei das Cäsium als interner Standardsubstanz dient.

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DETERMINATION OF LYSINE IN PROTEIN HYDROLYZATES USING LYSINE DECARBOXYLASE FROM *SALMONELLA HADAR*

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(Received August 13th, 1959)

Chemical, microbiological and enzymatic methods for the estimation of lysine in proteins have been described[1-3]. The chemical methods are rather cumbersome, while the bacteriological methods are time-consuming. The enzymatic assay involves the use of lysine decarboxylase in acetone–ether-dried preparations from *Bacterium cadaveris*[4-6]. The arginine decarboxylase which is also contained in these preparations is destroyed by keeping them at 0° for several days. Checking the preparations for arginine decarboxylase activity before use has been recommended[5].

Our studies on amino acid decarboxylases of *Salmonella hadar* revealed that when this microorganism was grown under suitable conditions, its cell-free extracts contained only lysine decarboxylase. A method for the determination of lysine in protein hydrolyzates based on these findings is described in the present paper.

EXPERIMENTAL

Growth of bacteria and preparation of cell-free extracts

Salmonella hadar, strain 1281[7]*, was grown in the following medium: trypticase soy broth, 1%; NaCl, 0.5%; Na_2HPO_4, 0.25%; NaH_2PO_4, 0.25%; Bovril, 0.3%; L-lysine monohydrochloride, 1%**. The pH was adjusted to 6.2–6.5.

Three successive passages of *Salmonella hadar* were made in tubes containing 5 ml of the medium. The tubes were incubated for 24 h at 25° under a layer of liquid parraffin[8]. After the third passage, the bacteria were inoculated into Erlenmeyer flasks containing 100 ml of the medium and were incubated for 24 h at 25° under liquid paraffin. The cells were centrifuged, washed twice and resuspended in 15 ml of distilled water. For the preparation of cell-free extracts, 15 ml of such suspensions were held in a 9 kc Raytheon sonic oscillator for 60 min. Bacterial debris was removed by centrifugation at 18,000 g for 15 min and the supernates were kept at 3–5°.

Protein hydrolysis

One gram of protein was heated under reflux with 50 ml of 6 *N* hydrochloric acid in a stirred oil bath at 120–125° for 35 h. The hydrolyzates were concentrated in vacuo at 50°, some water was added and the solution was again evaporated in vacuo, this procedure being repeated three times in all. The residue was dissolved in a small amount of 0.1 *M* citrate buffer, pH 5, the pH was adjusted to 5 by addition of NaOH and the solution was diluted to 25–100 ml by addition of 0.1 *M* citrate buffer, pH 5.

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* Obtained from the Central Laboratories, The Ministry of Health, Jerusalem.

** If lysine is omitted from the medium, the cell-free extracts contain arginine decarboxylase in addition to lysine decarboxylase.

Determination of lysine

The lysine content of the hydrolyzates was estimated in a Warburg apparatus at 37°. The main compartment of the vessels contained 2 ml of hydrolyzate or 1 ml of hydrolyzate and 1 ml of citrate buffer, pH 5. The side arm contained 0.5 ml of cell-free extract. Maximum output of CO_2 was obtained after about 45 min. Control experiments with KOH in the center well showed that no oxygen uptake occurred.

TABLE I

LYSINE CONTENT OF PROTEINS (PER CENT)[a]

Protein[b]	*Found in 3 separate hydrolyzates*	*Average*	*Previous findings*[c]
Human serum albumin	11.7; 11.6; 11.8	11.7	11.5–13.7
Casein	9.3; 9.4; 9.7	9.5	7.0– 9.8
Edestin	2.7; 2.3; 2.8	2.6	1.7– 2.8
Zein	0.07; 0.06; 0.07	0.07	0 – 0.2
Human hair	2.7; 2.8; 2.5	2.7	1.9– 4.2

[a] The values found are given for the dry protein. Moisture was estimated by drying the proteins in vacuo over phosphorus pentoxide at 100°.

[b] Human serum albumin was kindly supplied by the Blood Fractionation and Plasma Drying Institute, Tel-Aviv-Jaffa. Casein, edestin and zein were purchased from the Nutritional Biochemicals Corporation, Cleveland, Ohio. Human hair was obtained from a barber's shop.

[c] Figures taken from BLOCK AND WEISS[2] (pp. 252; 266; 278; 308; 316).

RESULTS

The results obtained with 5 proteins are given in Table I. They are well within the range of values previously obtained by other methods.

Preliminary experiments with solutions of pure L-lysine gave the expected theoretical values, while the following amino acids were not decarboxylated: glycine, L-alanine, L-serine, DL-valine, L-leucine, DL-isoleucine, L-cysteine, L-cystine, L-threonine, L-methionine, L-glutamic acid, L-aspartic acid, L-tyrosine, L-phenylalanine, L-tryptophan, L-histidine, L-proline, L-hydroxyproline, L-arginine, DL-citrulline, and DL-ornithine.

Additional evidence for the accuracy of the method was given by the following experiment. A part of the hydrolyzates of 2 proteins (human hair and human serum albumin) was run through a Decalso column which adsorbs only arginine and lysine[9]. The 2 amino acids were subsequently eluted. The lysine values for the 2 proteins, as estimated in the eluates, were 2.7 and 12.0%. The corresponding values found in the untreated parts of the hydrolyzates were 2.5 and 11.6%.

SUMMARY

Lysine may be determined in protein hydrolyzates with the aid of lysine decarboxylase contained in cell-free extracts of *Salmonella hadar* grown under suitable conditions.

RÉSUMÉ

La lysine peut être dosée dans des hydrolysats de protéines à l'aide de la lysine-décarboxylase, contenue dans des extraits de *Salmonella hadar*, cultivés dans des conditions appropriées.

ZUSAMMENFASSUNG

Lysin kann in Proteinhydrolysaten mit Hilfe einer Lysin-decarboxylase bestimmt werden, die in Extrakten von geeignet gezüchteten *Salmonella hadar*-Bakterien enthalten ist.

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REVUES DE LIVRE

Les réactions électrochimiques (Les méthodes électrochimiques d'analyse) par G. Charlot, Mme. J. Badoz-Lambling et B. Trémillon, Masson et Cie, édit. Paris 1959, 396 p., 407 figures, Broché 6.000 fr., Cartonné toile 6.800 fr.

Le Professeur Charlot vient de faire paraître un ouvrage qui aura — nous en sommes certains — un très grand retentissement parmi les analystes. Il nous avait déjà donné, dans le même genre, il y a quelques années: ,,L'analyse des réactions en solution''; on sait que de nombreux chercheurs se sont inspirés de ce livre pour leurs travaux. Cette fois, le Professeur Charlot et ses collaborateurs ont choisi comme thème les réactions électrochimiques et les méthodes d'électroanalyse, sujet combien redoutable pour ceux qui sont chargés de cet enseignement. Mais leur tâche sera désormais grandement facilitée s'ils veulent se donner la peine d'étudier la substance de cet ouvrage. Les chimistes d'autre part pourront acquérir des bases solides et véritablement générales qui leur permettront de résoudre sans difficulté la plupart des problèmes qui se poseront à eux. En effet, les plus grandes difficultés que l'on rencontre dans ce domaine proviennent du manque de coordination entre les différents chapitres qui le constituent, ce qui empêche d'en avoir une vue d'ensemble. Cette lacune vient d'être comblée. Quelques esprits chagrins reprocheront peut-être aux auteurs un excès de concision, mais avec un peu d'habitude, ce fait n'enlève rien à la clarté de l'exposé.

Citons les chapitres les plus importants de cet ouvrage: les réactions électrochimiques qualitatives et quantitatives et les courbes potentiel–courant au cours des réactions chimiques, le cas des réactions rapides et celui des réactions lentes, l'influence des facteurs physiques sur les phénomènes électrochimiques, la détermination expérimentale des courbes intensité–potentiel. Puis viennent les applications à la potentiométrie, à l'ampérométrie, à la coulométrie. Un chapitre spécial est consacré aux méthodes électrochimiques les plus récentes telles que la chronopotentiométrie, la chronoampérométrie, les diverses méthodes polarographiques oscillographiques et alternatives et la polarographie par redissolution anodique. Enfin, dans un dernier chapitre intitulé: ,,solvants variés'', les auteurs examinent le comportement des propriétés électrochimiques dans divers milieux et appliquent ces considérations aux méthodes physicochimiques d'analyse.

Dans ce livre, tout est neuf et on ne sait ce qu'on doit le plus admirer, la manière toute nouvelle de concevoir le problème ou la façon remarquable de présenter l'exposé. Des considérations générales, découlent le principe et l'interprétation de toutes les méthodes d'électroanalyse. Le Professeur Charlot et ses collaborateurs ont fait un travail considérable. On ne saurait trop recommander ce livre à tous ceux qui, de près ou de loin, s'intéressent à cette discipline.

D. Monnier (Genève)

Anorganische qualitative Mikroanalyse, von HANS MALISSA, Düsseldorf und A. A. BENEDETTI-PICHLER, New York. Mit 55 Textabbildungen. VIII, 333 Seiten, (Monographien aus dem Gebiete der qualitativen Mikroanalyse) Herausgegeben von A. A. BENEDETTI-PICHLER, New York 1959, Ganzleinen $ 11,65.

Ainsi que M. BENEDETTI-PICHLER l'annonce dans sa préface, ce livre inaugure une nouvelle série de monographies, destinée aux chimistes analystes et dont les trois premiers volumes seront consacrés à la microanalyse qualitative en général.

L'ouvrage que nous avons en mains concerne plus spécialement l'analyse minérale. Le suivant traitera de la microanalyse organique, tandis-que le troisième s'intitulera: ,,*Manipulateurs mécaniques en analyse chimique. Modes opératoires à l'échelle du microgramme*''.

Le but principal de ces livres est de donner aux lecteurs une vue d'ensemble des microméthodes actuellement utilisées, en développant suffisamment les détails des modes opératoires proposés, ce qui — selon l'auteur — n'est pas le cas des nombreux traités existant déjà.

Sans pouvoir partager entièrement cet avis, nous tenons néanmoins à saluer ici cette initiative, car nous estimons que toute oeuvre de récapitulation est fort utile de nos jours, en raison du développement prodigieux de la science.

Une brève analyse du contenu permettra à nos lecteurs d'apprécier les nombreuses qualités de ce livre.

L'introduction comprend un aperçu historique succint, les définitions actuelles de la sensibilité, spécificité et sélectivité des réactions, ainsi que quelques recommandations concernant la pureté des réactifs et le choix des ustensiles.

Le second chapitre, intitulé ,,Méthodes générales de travail'', traite successivement toutes les réactions effectuées au cours d'une analyse qualitative, sans en omettre les moins usuelles. Le lecteur trouvera suffisamment de détails pour qu'il puisse les appliquer sans trop de difficultés.

Le troisième et le quatrième chapitre sont tout spécialement consacrés à la technique des réactions d'identification. Le problème est examiné d'une manière que nous n'hésitons pas à qualifier de magistrale, dans ses généralités et dans ses détails. Les tables des sensibilités des réactions, telles qu'elles ont été dressées par WENGER, DUCKERT ET RUSCONI, sont complétées par quelques réactions plus récentes. Suit, à la fin, une longue partie décrivant minutieusement les réactions d'identification principales de chaque élément.

L'ouvrage se termine par un grand chapitre comprenant l'exécution d'une analyse qualitative. Après une énumération des essais préliminaires les plus variés, les auteurs exposent deux schémas d'analyse (l'un pour les cations, l'autre pour les anions) basés sur les modes opératoires de NOYES ET BRAY. Ici encore les possibilités d'application de la méthode sont discutées sur une base scientifique, incitant l'analyste à travailler d'une façon intelligente et éclairée et non pas à effectuer des opérations de ,,cuisine'' en se basant aveuglement sur des ,,recettes'' sacrées.

Le chapitre se termine avec quelques prescriptions relatives à l'analyse des aciers, des peintures (tableaux), des verres, des glaçures, des objets en céramique et des silicates. Quelques pages, enfin, sont encore consacrées à l'analyse des poussières et à la recherche des éléments dans les produits organiques.

Bien que la réputation des auteurs se passe de tout commentaire, nous tenons à faire ici l'éloge de cet excellent ouvrage, dans lequel la théorie s'allie à la pratique d'une manière originale, propre à M. BENEDETTI-PICHLER, et nous nous faisons un plaisir de reconnaître que ce livre jette une nouvelle lumière dans le domaine de la microanalyse. Persuadé du succès qu'il emportera, nous souhaitons tout simplement que les volumes suivants de cette série soient à la même hauteur.

I. KAPÉTANIDIS (Genève)

Communication

Mr. W. J. PARKER has resigned his position as Secretary of the Polarographic Society. Mr. J. H. GLOVER has been co-opted as Secretary and all communications to the Society including subscriptions should be sent direct to him at:

75, Craven Gardens, Wimbledon, S.W. 19. Great Britain.

TITRATION OF MERCURY(II) WITH SODIUM TETRAPHENYLBORON*

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(Received September 23rd, 1959)

During an investigation concerning the possibilities of a mercurimetric titration of the insoluble tetraphenylboron precipitates of potassium and of some organic bases, the reaction of sodium tetraphenylboron with mercuric and mercurous ions was studied. There is in the literature some controversy on the nature of the precipitates resulting from the reaction. The end-product of the reaction of an excess of mercuric ions with tetraphenylboron is known to be a phenylmercuric salt[1], but some workers consider that during the reaction mercuric or mercurous tetraphenylboron is formed[2,3]. We have found that the titration of tetraphenylboron with mercuric salts (nitrate, perchlorate) proceeds in two steps. In the first step of the titration, which can be followed up by potentiometry, polarometry or polarography[4], 3 equivs. of mercury(II) are consumed per mole of tetraphenylboron with the formation of diphenylmercury and phenylboric acid[5]. The mercuric tetraphenylboron reported in the literature[2] is in fact diphenylmercury and consequently the mercurous tetraphenylboron of the literature[2] is a mixture of diphenylmercury and metallic mercury. Mercury tetraphenylboron, if any is formed during the titration, must be extremely quickly decomposed to diphenylmercury and phenylboric acid. In the second step of the titration the added mercuric ions react with diphenylmercury and with phenylboric acid, and the corresponding phenylmercuric salt is found after a consumption of a total of 8 equivs. of mercury(II) per mole of tetraphenylboron[4,5]. The insoluble diphenylmercury which separates in the first step dissolves again during the second step and the solution at the end-point is clear, when the titration is performed with mercuric nitrate or perchlorate, since phenylmercuric nitrate and perchlorate are sufficiently soluble in water.

In the reverse titration, when mercury(II) is titrated with a solution of sodium tetraphenylboron, two steps are again noted[4-6]. In the first, 0.25 mole of sodium tetraphenylboron are consumed per mole of mercury(II), phenylmercuric salt is formed and the liquid remains clear. In the second step, phenylmercuric salt reacts with the titrant and the solution becomes turbid. Insoluble diphenylmercury separates, until about 0.5 mole of tetraphenylboron are consumed according to:

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[*] This paper is a part of the communication read at the Third Congress of Analytical Chemistry, Prague, 1-8 September 1959.

$$4\ Hg(NO_3)_2 + Na[B(C_6H_5)_4] + 3\ H_2O = 4\ C_6H_5HgNO_3 + NaNO_3 + 3\ HNO_3 + H_3BO_3$$

(first step)

$$4\ C_6H_5HgNO_3 + Na[B(C_6H_5)_4] + 3\ H_2O = 4\ C_6H_5HgC_6H_5 + NaNO_3 + 3\ HNO_3 + H_3BO_3$$

(second step)

At present the literature on sodium tetraphenylboron is concerned primarily with the determination of potassium, ammonium and organic bases. It seemed interesting to extend the use of the reagent to the direct titration of mercury. A gravimetric determination of mercury in the form of diphenylmercury after precipitation with sodium tetraphenylboron has already been described from this laboratory[5].

EXPERIMENTAL

Reagents

0.020 *M* sodium tetraphenylboron was prepared by dissolving about 2 g of reagent grade sodium tetraphenylboron "Kalignost" in twice distilled water, clearing with alumina if turbid, and making up to 250 ml with twice distilled water. The titre of the solution was determined by titrating a standard solution of mercuric nitrate as described in the procedure. An appropriate volume of water was then added to obtain a 0.020 *M* solution. Alternatively the titre was checked by potentiometric titration with silver nitrate[7]. The solution was stable for a week or more, provided that its pH was about 8.5. The titre should be checked daily.

0.16 *N* mercuric nitrate, containing 16.0488 mg of Hg/ml, was prepared by dissolving the exactly weighed amount of thrice distilled metallic mercury in concentrated nitric acid, boiling to expel nitrogen oxides and diluting to volume with twice distilled water.

Procedure

An aliquot of the sample was diluted to contain about 5–50 mg of mercury(II) and not more than 1 mg/ml, and titrated under constant stirring with the solution of sodium tetraphenylboron from a microburet. After the addition of each drop of titrant, a turbidity of diphenylmercury developed but rapidly dissolved on swirling. When all the mercury had been converted to phenylmercuric nitrate, the excess of titrant caused a persistent turbidity of diphenylmercury. The end-point was sufficiently sharp and could be recognized within 0.01 ml of the titrant.

1 mole of sodium tetraphenylboron corresponds to 4 moles of mercury(II), hence 1 ml of 0.020 *M* sodium tetraphenylboron corresponds to 16.0488 mg of mercury(II).

The titration could be performed in neutral or slightly acidic (up to 0.05 *N* HNO_3 or $HClO_4$) solutions or in solutions buffered with sodium acetate. The correct dilution of the sample was important. When it was not diluted sufficiently, amorphous or crystalline particles of phenylmercuric nitrate separated during the titration, making the exact recognition of the end-point difficult and causing low results. These particles however could readily be differentiated from the turbidity of diphenylmercury. Provided that the dilution of the sample was satisfactory, the volume of the titrated solution was not critical. In actual experiments about 15 ml were used for 5-10 mg of mercury(II), about 40 ml for 5–30 mg and about 60 ml for 5–50 mg. When greater amounts of mercury(II) were present, correspondingly larger volumes had to be used for the titration.

Interferences

In solutions buffered with sodium acetate the interferences of several ions could be eliminated by a suitable chelating agent. When ethylenediaminetetraacetic acid was added, mercury could be titrated in the acetate medium even when an excess of Cu, Zn, Mg, Ca, Mn, Ni, etc, was present.

In a slightly acidic solution no interference was observed from Zn, Cu, Ba, Ni, Ca, Fe, Co, Pb, Al, Bi, etc.

Common anions (NO_3^-, ClO_4^-, PO_4^{-3}, ClO_3^-, SO_4^{-2}, NO_2^-, $B_4O_7^{-2}$, AsO_4^{-3}) did not interfere. Any anion which gives insoluble phenylmercuric salts (Cl^-, Br^-, I^-, CNS^-) caused a turbidity at the beginning of the titration making the determination impossible.

Mercury(I) gave at the beginning of the titration a fine gray precipitate of metallic mercury and made the determination difficult.

Any ion which precipitates with sodium tetraphenylboron interfered when present in excess of the mercuric ions. However, in slightly acidic solution the titration gave good results even when the amount of potassium present was 2–3 times that of mercury(II). On the other hand, silver ions could be tolerated only when the amount was about half that of mercury(II). Obviously, the affinity of the tetraphenylboron complex for mercuric ions is markedly higher than that for the other ions. For example, when a solution of potassium and mercuric ions was titrated with sodium tetraphenylboron, the added reagent was first rapidly decomposed by mercuric ion, forming phenylmercuric salt, then phenylmercuric salt reacted to form diphenylmercury and in fact no tetraphenylboron was available to precipitate potassium. When all the mercury present has been bound as diphenylmercury, the titrant no longer reacted with it and insoluble potassium tetraphenylboron could separate. With relatively high concentrations of potassium, some insoluble tetraphenylboron was precipitated simultaneously with the formation of phenylmercuric salt; this reacted only slowly with the mercury(II) present. Silver tetraphenylboron is much more insoluble than the potassium compound, therefore silver interferes in markedly lower concentrations.

RESULTS

Numerous titrations of standard solutions of mercuric nitrate and mercuric perchlorate were performed. Some figures are presented in the table. The error did not usually exceed 1%. When the content of mercury was determined by the present method in various materials, *e.g.* mercuric compounds, organic mercurials and

TABLE I

Hg taken mg	*0.020 M sodium tetraphenylboron consumed* ml	*Hg found* mg	*Difference* %
2.0	0.12	1.93	— 3.50
2.0	0.13	2.08	+ 4.00
5.0	0.31	4.98	— 0.40
5.0	0.31	4.98	— 0.40
10.0	0.63	10.10	+ 1.00
10.0	0.62	9.95	— 0.50
15.0	0.93	14.93	— 0.50
15.0	0.94	15.08	+ 0.50
20.0	1.24	19.90	— 0.50
20.0	1.25	20.05	+ 0.25
25.0	1.56	25.00	± 0.00
25.0	1.57	25.20	+ 0.75
30.0	1.87	30.00	± 0.00
30.0	1.87	30.00	± 0.00
30.0	1.86	29.90	— 0.30

pharmaceutical preparations after a suitable mineralisation, the results obtained agreed well with those obtained by the standard titrimetric procedure using thiocyanate.

ACKNOWLEDGEMENT

The author is indebted to Dr. H. BÜECHL of Heyl & Co., Hildesheim (Germany) for supplying the sodium tetraphenylboron ("Kalignost") used in this work.

SUMMARY

A direct visual titration of mercury (II) with sodium tetraphenylboron ("Kalignost") is described. Phenylmercuric salts are formed and the end-point is indicated by a turbidity of insoluble diphenylmercury.

RÉSUMÉ

Une méthode est décrite pour le titrage direct du mercure(II) au moyen de tétraphénylborate de sodium. La formation de diphénylmercure, insoluble, indique le point final.

ZUSAMMENFASSUNG

Es wird eine direkte Titration der Quecksilber(II)-Ionen mit Tetraphenylbornatrium („Kalignost") beschrieben. Der Endpunkt ist erreicht, sobald sich die Lösung durch Ausscheidung von Diphenylquecksilber zu trüben beginnt.

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DETERMINATION OF PROTACTINIUM-233 IN IRRADIATED THORIUM

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The increasing interest in the ^{233}U/^{232}Th fuel cycle for future reactors stresses the importance of being able to determine ^{233}U in thorium, since the rate of production of ^{233}U is a vital step in the analysis of performance of experimental assemblies. Neutron capture in ^{232}Th produces the sequence:

$$^{232}\text{Th}\ (n, \gamma)\ ^{233}\text{Th} \xrightarrow[\text{23.3 min}]{\beta} {}^{233}\text{Pa} \xrightarrow[\text{27.4 days}]{\beta} {}^{233}\text{U}\ (1.62 \cdot 10^5\ \text{years})$$

^{233}Th is rather short-lived and cannot be separated chemically from ^{232}Th, while ^{233}U has a low specific activity on account of its long half-life. The intermediate daughter ^{233}Pa is therefore chosen for the assessment during the initial stages of a reactor or experimental assembly, before any appreciable amount of ^{233}U has grown in. The method was designed to separate amounts ranging from 200–10^5 d.p.m. of ^{233}Pa in 1-g portions of irradiated thorium metal containing 10^4 to 10^9 fissions. The yield of the chemical process was determined from the recovery of ^{231}Pa tracer added in known amount. On account of the low activity of some of the samples to be analysed, it was desirable to use a fairly simple chemical separation scheme giving a high yield. Good decontamination was essential, since in the presence of the 27.4 day ^{233}Pa, any β-emitting long-lived impurity would not be detected easily without prolonged counting of the final sources.

Owing to the ease with which protactinium hydrolyses and forms adsorbable colloids in aqueous solution, it is necessary to carry out chemical processes in strong acid or complexing solutions using polythene apparatus. Solvent extraction and ion exchange are attractive methods under these conditions. A number of organic solvents are available for the extraction of protactinium from strong acid solution and are discussed by KATZ AND SEABORG[1] and HYDE[2].

Di-isopropyl carbinol was considered to be the most suitable solvent for the scheme on account of its efficiency for protactinium and high selectivity in strongly acid systems. Protactinium is strongly adsorbed on anion-exchange resin (*e.g.* Amberlite C.G. 400) from 6 N hydrochloric acid and is easily eluted by the same acid containing 0.5 N hydrofluoric acid[3].

For the measurement of the ^{233}Pa radiation, β-counting was preferred rather than γ-counting since the latter required a higher source activity and more elaborate equipment for accurate determination.

The β-rays of ^{233}Pa are of low energy and are accompanied by large numbers of conversion electrons. The efficiency of end-window counters for this type of emission cannot be calculated accurately from geometrical consideration and calibration by some other counting method must be used. The method reported here is similar to that described by CRIPPS AND WEALE[4] for the absolute counting of ^{239}Np and that of McISAAC AND FREILING[5] for ^{233}Pa, involving a source of ^{233}Pa in equilibrium with its parent ^{237}Np whose disintegration rate was determined accurately by α-counting. Calibration of an end-window gas flow proportional counter using this source gave good agreement with the efficiency obtained using a pure ^{233}Pa source which had been standardised by 4π-counting. Since the final sample sources contained added ^{231}Pa, these and the standard ^{237}Np source were β-counted using a 5 mg/cm^2 absorber to cut out the alpha particles.

EXPERIMENTAL

Chemical

For the development of the scheme, synthetic solutions of 1 g of thorium in 3 ml of 6 M nitric acid containing a known amount of ^{231}Pa tracer (about 200 d.p.m.) and some 24 h old fission products equivalent to 5×10^{12} fissions were prepared. The solvent extraction stage showed a 90% yield for the ^{231}Pa but produced sources contaminated with about 2×10^4 d.p.m. of β–γ radiation most of which appeared to be ^{99}Mo, ^{97}Zr and ^{95}Zr. These impurities were removed by passing the solution in 6 N hydrochloric acid through an anion-exchange column which retained only the protactinium and molybdenum and by eluting the protactinium with 6 N hydrochloric acid containing 0.5 N hydrofluoric acid which removed the protactinium as the fluoride complex leaving the molybdenum on the column[3]. After this stage resultant sources contained about 1.5×10^3 d.p.m. of impurities and the decay curves showed two components having half lives of 70 min and about 20 h respectively, the former being predominant. Since over 24 h had elapsed from the last time of irradiation the short-lived component must have separated from a longer lived parent during the chemical purification. Examination of possible fission product species and their yields showed that the short-lived component must be due to ^{97}Nb, the daughter of 17 h ^{97}Zr, the latter species accounting for the longer-lived component.

After a few days these activities decayed leaving a residual long-lived β-emitter of about 90 d.p.m. The decontamination achieved was considered satisfactory for samples containing the larger amounts of ^{233}Pa and fission products. By increasing the concentration of the hydrochloric acid in the eluting mixture to 11 N all niobium should be held on the column since the distribution coefficient for the adsorption of Nb^{+5} is about 60 at this concentration as against 6 for 6 N hydrochloric acid–0.5 N hydrofluoric acid mixture[3].

Repeated experiments with varying amounts of fission products added gave sources which showed a constant activity of about 30 d.p.m. due to the γ-radiation of the ^{231}Pa tracer. Examination of the complex decay scheme of this isotope made it clear that conversion electrons and the X-rays produced by the L-shell conversion of the gamma rays in the 27–46 keV region would give counts in the β-counter equivalent to about 10% of the alpha disintegration rate. Since these counts were proportional to the alpha radiation of the tracer, the ratio was determined experimentally and allowed for in the final sources.

Counting of the sources

By 4π-counting

^{233}Pa was obtained by irradiation in B.E.P.O. Harwell of thorium nitrate (AnalaR) and purified by the above chemical method. Sources were prepared by weighing out portions of the ^{233}Pa solution onto thin plastic foils (VYNS)[4] and also onto stainless steel discs.

The VYNS sources were counted in a $4\pi\,\beta$-counter (A.E.R.E. Type 1364) assuming an efficiency of 100%. This assumption is based on the results of PATE AND YAFFE[7] who showed that the efficiency for this type of counter with β-emission of similar energy is about 99%. As the β-emission is accompanied by coincident conversion electrons which are counted with high efficiency, the overall efficiency of the 4π counter must be greater than this. Comparison of the steel disc sources with the 4π sources gave an efficiency of 0.287 ± 0.01 for the 2-in. diameter end-window counter, with the source at a distance of 1 cm.

By ^{237}Np

Stainless steel disc sources were prepared from a solution of ^{237}Np containing ^{233}Pa in equilibrium and standardized by comparison with a stronger alpha source mounted similarly, and of known disintegration rate, in an α-scintillation counter (A.E.R.E. Type 1093). From the β-count rate of these steel disc sources, the end-window counter efficiency was found to be 0.296 ± 0.008. These results compare favourably with later work by BROWN AND LARGE[8] whose similar experiments gave an efficiency of 0.307 ± 0.004 for the 4π calibration and an efficiency of 0.299 ± 0.006 using a ^{237}Np – ^{233}Pa source. The 4π results have a larger scatter than those of the ^{237}Np – ^{233}Pa, due to the greater sensitivity of the 4π counter to differences in source thickness, but the results agree within experimental error. During their experiments, BROWN AND LARGE purified some of the ^{237}Np and allowed the ^{233}Pa to grow into equilibrium, in order to check the purity of the source, and their results confirmed the validity of the method.

In the final sources the chemical yields of the analyses were found by α-scintillation counting of the recovered ^{231}Pa.

EXPERIMENTAL

Apparatus

Polythene ion-exchange columns containing Amberlite C.G. 400 resin, volume 50 mm × 4 mm, previously conditioned with 6 *N* hydrochloric acid. Small polythene beakers of 10-ml capacity. All solvent extractions and washings carried out in 5-ml polythene ampoules drawn out to a spout[6]. Lustroid tubes of 3-ml capacity for transfer of liquid phases. Stainless steel discs of 1 in. diameter. End-window proportional β-counter. Alpha scintillation counter. A standardized source of ^{237}Np in equilibrium with its ^{233}Pa daughter.

Reagents

Concentrated nitric acid containing the equivalent of 0.01 *N* hydrofluoric acid, 6 *N* hydrochloric acid containing the equivalent of 0.5 *N* hydrofluoric acid, 11 *N* hydrochloric acid containing the equivalent of 0.5 *N* hydrofluoric acid.

Di-isopropyl carbinol saturated with 6 *M* nitric acid. Pure ^{231}Pa tracer solution standardized.

Procedure

Add about 1 g of the irradiated thorium metal and a known amount of ^{231}Pa tracer (about 200 d.p.m.) to concentrated nitric acid containing the equivalent of 0.01 *N* hydrofluoric acid in a platinum dish. Dissolve the metal by heating, adding more acid when necessary. Evaporate the final solution to about 1 ml and dilute with water to 3 ml. Extract the protactinium by twice shaking for two minutes with 1 ml of di-isopropyl carbinol equilibrated with 6 *M* nitric acid, and wash the combined organic phase three times with 1 ml 6 *N* hydrochloric acid. Back extract the protactinium by shaking twice for two minutes with 1 ml of 6 *N* hydrochloric acid – 0.5 *N* hydrofluoric acid mixture, wash the combined aqueous phase with 1 ml of the organic reagent, and discard the latter. Evaporate the aqueous solution to dryness in a small polythene beaker on a water bath and using a jet of air. Dissolve the residue in 1 ml of 6 *N* hydrochloric acid and put through the anion-exchange column, followed by a further 6 ml of 6 *N* hydrochloric acid and reject the effluent. Elute the protactinium using 3 ml of 11 *N* hydrochloric acid – 0.5 *N* hydrofluoric acid mixture and evaporate the effluent to dryness in a polythene beaker. Dissolve the residue in a small amount of 6 *M* nitric acid, and evaporate on a 1-inch stainless steel disc.

Determine the disintegration rate of the source by counting the ^{233}Pa β-emission in an end-window β-counter with a 5 mg/cm^2 absorber, and comparing with a similarly mounted standard source of ^{237}Np of known activity in equilibrium with its ^{233}Pa daughter.

Count the source in an α-counter and determine the disintegration rate of the recovered ^{231}Pa. This compared with the original amount put in will give the factor required to convert the ^{233}Pa disintegration rate into the absolute amount present in the original sample.

Note: A source of the ^{231}Pa should be prepared, and β-counted in order to determine the contribution of the γ-emission. This is proportional to its α-disintegration rate and the amount may therefore be calculated for the appropriate quantity of tracer in each sample and deducted from the total β-count.

RESULTS AND CONCLUSIONS

The initial experiments showed that there was adequate decontamination to allow the ^{233}Pa to be directly counted. However in order to allow for any losses during the chemical separation it was essential that complete isotopic exchange between the ^{231}Pa and the ^{233}Pa was obtained during the initial dissolution. Although this was fairly certain since protactinium usually exists as Pa^{+5} in strongly acid solution, some test runs were made in order to confirm the exchange.

Known amounts of ^{233}Pa obtained by the irradiation of thorium were added to 1-g samples of thorium metal, together with ^{231}Pa during dissolution. If isotopic exchange occurred, then the known initial ratio of ^{233}Pa/^{231}Pa should also be found in the final sources.

TABLE I

Sample No.	*Added initially d.p.m.*		*Recovered d.p.m.*		$\frac{b}{a} = x$	$\frac{b_1}{a_1} = y$	$\frac{y}{x}$
	^{231}Pa (a)	*^{233}Pa (b)*	*^{231}Pa (a_1)*	*^{233}Pa (b_1)*			
1	426	56000	257	33000	131.500	128.400	0.977
2	360	15500	292	12400	43.050	42.460	0.986
3	389	3080	210	1680	7.918	8.000	1.010
4	300	1140	204	749	3.800	3.672	0.966
5	373	572	333	496	1.531	1.490	0.974
6	357	140	170	68.5	0.392	0.403	1.027
						mean	0.990 ± 0.024

In Table I the last column shows the initial and final ratios compared. The average value is 0.990 with a standard deviation of 2%, and allowing for the usual counting errors, this shows that isotopic exchange was obtained.

The chemical method given above is simple and rapid, and gives a decontamination of 10^6 at 24 h after irradiation, with a known yield of 70–80% determined by the addition of ^{231}Pa tracer. Sources on stainless steel discs are easily prepared and may be counted in an end-window counter provided there is sufficient thickness of absorber to prevent ^{231}Pa α-particles from entering the counter. Allowances must be made for the contribution of ^{231}Pa gamma activity to the β-count rate. The absolute disintegration rate may be obtained by comparison with a standardized source of ^{237}Np–^{233}Pa which constitutes a permanent standard for the calibration of end-window counters.

ACKNOWLEDGEMENTS

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SUMMARY

A method has been devised for the absolute determination of ^{233}Pa in irradiated thorium metal by counting the β-emission of chemically separated and purified sources. The counter was calibrated by a source of ^{237}Np of known activity in equilibrium with its ^{233}Pa daughter, and checked by 4 π counting.

RÉSUMÉ

Les auteurs ont établi une méthode de dosage de ^{233}Pa dans le thorium irradié par comptage des rayons β. Le compteur est calibré par une source de ^{237}Np, d'activité connue, en équilibre avec ^{233}Pa.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von ^{233}Pa in bestrahltem Thorium durch Zählung der β-Emission. Die Eichung des Counters erfolgte mit einer Quelle von ^{237}Np bekannter Aktivität im Gleichgewicht mit ^{233}Pa.

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SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM IN AIR AND DUST

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INTRODUCTION

It is well known that the handling of beryllium and its compounds can give rise to very serious health hazards, if most stringent precautions are not taken. In any laboratory or workshop where beryllium is handled, it is very important that all operations should be monitored to ensure that the operators are not subjected to more than a permitted dosage of beryllium.

The whole problem is discussed by BROOKS[1].

The most serious hazard in the handling of beryllium is due to deposition of beryllium compounds in the lungs, causing either acute or chronic berylliosis. Surface contamination can also be hazardous, because it is a potential source of aerial contamination, and also because beryllium compounds on the skin can set up a very unpleasant dermatitis, especially if they come into contact with cuts or abrasions. Monitoring therefore takes two forms: samples of air are taken to ensure that the level of aerial contamination is very low (see later), and samples of dust are taken from surfaces at appropriate positions.

The collection of samples from surfaces is a fairly simple procedure. A known area of the surface, usually 1 m^2, is wiped carefully with a filter paper (a 5.5 cm Whatman No. 541 paper is suitable), when any loosely adhering deposit is transferred to the paper. This is then placed in a suitable container (*e.g.* a polythene envelope) and taken to the analytical laboratory. The maximum acceptable level for surface contamination is a matter for debate, and various factors must be taken into consideration in setting a limit for any particular type of surface.

Definite maximum permissible levels for beryllium in air have been recommended by the United States Atomic Energy Commission[2] and have been widely accepted in this country. These are that:

a. The concentration of beryllium in air should not exceed an average of 2 μg/m^3 over an 8-h working day in areas where beryllium is being handled.

b. The concentration of beryllium in air should not exceed 25 μg/m^3 for any period however short.

c. The average concentration per month of beryllium in air, in the neighbourhood of an area where beryllium is handled, should not exceed 0.01 μg/m^3.

It is therefore obvious that the taking of suitable air samples presents a considerable problem. Each one of these specifications requires special consideration.

To meet the first requirement, ideally it would be necessary to take a sample of air over a period of 8 h at a carefully maintained constant flow, collect all the dust and show that there was less than 2 μg/m^3 Be present. In practice, however, this is not usually done, a 4–5 h sample being considered sufficient to give a reasonable picture of average atmospheric contamination. A rapid method of analysis is not essential in this instance.

To meet the second requirement, ideally it would be necessary to have continuously recording monitors to register instantaneously any contamination greater than 25 μg/m^3. Such a monitor has been described by GILLIESON AND CHURCHILL[3], but its reliability has been questioned on the grounds that the response is dependent on the particle size of the dust, and so an absolute measure of the beryllium concentration cannot be obtained. It is moreover, a very expensive instrument. In practice, therefore, a sample is taken over as short a period as possible, bearing in mind the limit of sensitivity of the analytical method being used. A rapid method of analysis is essential if any action is to be taken as a result of this analysis.

To meet the third requirement ideally, one would take samples of air over the monthly period and show that the average contamination was less than 0.01 μg/m^3. In practice, however, it is usual to take a sample over a period of at least 8 h, passing about 30–40 m^3 air through the dust collector. If several such samples are below the limit of 0.01 μg/m^3 it is reasonable to assume that a monthly average would also be below that level.

From the above considerations, various assumptions can be made as to the requirements of the analytical method.

a. The lower limit of sensitivity required is governed by the third specification ($<$0.01 μg/m^3). Since about 30–40 m^3 air are used, a lower limit of about 0.1 μg beryllium is sufficient to give a margin of about 25–30% of tolerance.

b. The method should be simple and rapid to meet as nearly as possible the requirements of the second specification (25 μg/m^3 for a short period). If 1 μg can be detected with certainty, then it would be only necessary to sample 0.04 m^3 air, *i.e.* for less than 1 min.

c. The method must be highly specific for beryllium, and this is specially important to meet the requirements of the third specification, when there will be gross dilution of any beryllium by ordinary dust constituents. (This is also an important factor in the analysis of smear samples).

d. The filter used in collecting the dust must:

1. Retain as many as possible of the particles of beryllium-bearing dust in the

particle size range 0.5–1.5 μ. These are thought to be of the greatest significance as a lung irritant.

2. Pass as fast a flow of gas as is possible, consistent with 1.

3. Not readily clog, as this would make it difficult to maintain a constant flow over a period of several hours.

Airborne dust collection

In most of the analysis so far carried out at Whetstone, samples of dust have been collected by passing air through a 5.5 cm No. 41 Whatman filter paper, at a rate of about 3–4 m^3/h using a Fleming Radio (Development) Ltd. Dust Sample Unit Type No. 1355 B. However, No. 41 Whatman filter papers are not ideal media for collecting dust samples. They have several disadvantages.

1. Two investigators[4,5] have shown that particles below 2 μ are not quantitatively retained, and we have confirmed this, (see later).

2. They have a marked tendency to clog up over an extended period, especially in dusty atmospheres.

3. They have certain disadvantages when a rapid method of analysis is required (see later).

They have the advantage of being cheap, readily available, and of having low mineral content.

We have recently investigated Membrane air filters, manufactured by the Membranfilter-gesellschaft, Göttingen, Germany*. These membranes have an extremely fine pore system, and act as mechanical sieves. They are synthetic cellulose-ester materials, and have several properties which make them very useful for air filtration.

a. The pore sizes are carefully controlled so that particles down to any given size can be quantitatively retained.

b. They show a marked resistance to clogging, and in this respect are greatly superior to filter paper.

c. They lend themselves to rapid analysis (see later).

Various porosities were examined, and of those tested AF 400 and AF 600 were the most useful.

The air flow through the filter is an important factor and Table I shows the volumes

TABLE I

COMPARISON OF FLOW-RATES OF VARIOUS FILTERS

Filter medium		*Volume of air in 10 min (m^3)*
Membrane filter	AF 600	1.48
	AF 400	0.65
	AF 150	0.11
Whatman filter paper	No. 41	1.13
	No. 40	0.51
	No. 542	0.12

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* Obtainable in Great Britain from Hudes Merchandising Co. London.

of air passed by various filters over a period of 10 min at a constant pressure difference. This indicates that AF 400 is nearly equivalent to No. 40 paper and AF 600 to No. 41 paper.

However, the position is rather different for tests taken over a longer period, as Table II shows. It will be seen that a direct comparison between Membrane filter AF 400 and filter paper No. 41 shows that initially the flow rate through the filter paper is much faster, but rapidly falls off, and over a period of three hours as much air is passed by the membrane filter as the filter paper. This is in spite of the fact that more dust was collected on the membrane filter then on the filter paper, as the weight of ash indicates.

TABLE II

COMPARISON OF FLOW-RATES OF FILTERS OVER A PERIOD OF TIME

Time	*Air passed in m^3 AF 400 membrane*	*Air passed in m^3 No. 41 paper*
30 min	1.7	2.5
1 hour	3.6	4.6
90 min	5.1	6.2
2 hours	6.5	7.4
2½ hours	7.7	8.3
3 hours	8.7	8.9
Weight of ash after 3 hours	4.5 mg	2.8 mg

Some tests carried out on the particle sizes of dust retained by the membrane filters indicated that the maker's claims (AF 400 retains particles $>0.5\,\mu$, and AF 600 retains particles $>1.0\,\mu$), were justified. When a No. 41 filter paper was placed in series with an AF 600 or an AF 400 membrane filter, a considerable number of particles passed through the filter paper and were retained on the membrane filters. It was also shown that a small number of particles passed through an AF 600 membrane filter, but were retained on the AF 400 filter. This indicates that the AF 400 filter is the more reliable, but where a fast flow rate is required, as in taking short-duration samples, the AF 600 filter is preferable. It will be seen from the above consideration that membrane filters are preferable to filter papers on several counts; their only disadvantage is their relatively high cost.

Possible methods of analysis for beryllium

Several spectrographic methods[6-9], have been described for the determination of beryllium retained on dust filters. These methods have the advantage of specificity and speed. However, they have a relatively low precision, and if a considerable number of analyses are required, an expensive piece of apparatus is tied up. For theses reasons an alternative procedure was investigated.

Fluorimetric methods have been described by several authors[10-13].

However, these depend on an initial partial separation of the beryllium and are therefore time-consuming. Various spectrophotometric methods have also been described for the determination of beryllium, using such reagents as *p*-nitrobenzene-azo-orcinol, eriochrome cyanine-R, aurine tricarboxylic acid (aluminon), naphthazarin, quinalizarin, and naphthachrome Green G. However, various other metals interfere with the determination of beryllium using these reagents, including iron, cobalt, aluminium, titanium, zinc, zirconium, copper, vanadium and chromium. LUKE AND CAMPBELL[14] describe the use of aluminon for the determination of beryllium in beryllium copper, where interference due to other metals present in the alloy in small amounts is eliminated by complexing them with ethylenediaminetetracetic acid. This has been investigated as a possible technique for determining beryllium in dust samples. Preliminary experiments with aluminon (after purification by a special technique, described later) indicated that it was a sufficiently sensitive reagent for the purpose. Using 4-cm cells and a spectrophotometer at 5300 Å, a blank solution gave an optical density reading of 0.06; with 0.1 μg Be added the reading was 0.08; with 0.5 g Be the reading was 0.13; and with 1.0 μg Be the reading was 0.18. (In each case in 10 ml total volume). Above 8.0 μg Be there is a marked reduction in sensitivity, due to insufficient reagent being present, (using the quantity described later in the appendix). If more reagent is used, the blank reading is correspondingly higher.

These preliminary experiments led to further investigation and the procedure finally adopted was a modified "aluminon" method.

Preparation of the sample for analysis

There are two alternative methods of preparing the sample for analysis.

a. Dry ignition followed by solution of the ash.
b. Wet acid oxidation.

There is a slight preference for the former method since smaller quantities of reagents are used, so that the final analysis can be carried out on a small volume without the necessity of evaporation. Moreover, there is a possibility that calcined beryllium oxide may be present in the dust, and be insoluble in the acid solvent. In the ignition procedure, the filter paper is ignited at 800° in a silica crucible until there is no carbonaceous material remaining. (In the event of using membrane filters, it is only necessary to fold and apply a lighted match followed by a 30-sec ignition to remove last traces of organic matter, a far more rapid procedure than for filter papers.) The ash is fused at 600° with 0.25 g potassium bisulphate to ensure complete solution of the beryllium oxide. The melt is extracted with dilute hydrochloric acid—if silica precipitates at this stage, it is removed by centrifuging.

Interference due to other metals

All the metals normally found in atmospheric dust were tested for interference in the proposed procedure, using EDTA as a complexant. No interference was observed for calcium, magnesium, zinc, aluminium, titanium, cobalt, copper, vanadium or nickel in quantities up to 2 mg. Iron interfered very slightly, as its complex with EDTA absorbed very slightly at 5300 Å. However, compensation for this could very easily be made, when appreciable amounts were present, by measuring the absorption at 4200 Å and making an appropriate correction (see later).

Zirconium interfered very slightly, 1 mg Zr giving a colour equivalent to 0.6 μg Be, while chromium interfered considerably, 0.1 mg Cr giving a colour equivalent to

1.0 μg Be. Use is therefore made of the fact that both these metals form more stable complexes with nitrilotriacetic acid than with EDTA. By addition of this complexant, interference by zirconium is eliminated, and interference by chromium very markedly reduced, (0.5 mg Cr gives a colour equivalent to 0.3 μg Be). This can usually be neglected since chromium is not normally present in dust. If it should be present it would be readily detected since its complex with aluminon is a characteristic mauve colour, and a correction could be made by also measuring the absorption at 6000 Å, where the absorption due to beryllium is negligible, while the absorption due to chromium is a little less than at 5300 Å.

Development of the colour complex

To the acid solution of the potassium bisulphate fusion, EDTA and nitrilotriacetic acid solution are added, and the pH adjusted to the range of 4–7 with dilute ammonia. A buffered solution of aluminon is then added (pH 5.8). This pH was found to be the most suitable, combining the advantages of a low blank reading with maximum sensitivity for beryllium. The solution is then diluted to volume, colour development completed by heating in a boiling water bath for 10 min, the solution cooled and the absorption measured at 5300 Å. After a little experience, it is possible to estimate the approximate beryllium level by visible inspection immediately after adding the aluminon reagent, if a rapid "safety" check is required.

Time of analysis

Normally one analysis can be completed in 30 min after taking the sample, or four analyses in 45 min. However, this can be speeded up if an approximate figure is acceptable. A dust sample can be collected on an AH 600 membrane filter over 5 min taken to the laboratory ignited and fused with bisulphate in 2 min, cooled extracted with dilute acid in 2–3 min, and the colour developed in the cold and estimated visually in 2–3 min; a total time of about 15 min, or 7 min after the sample has been received in the laboratory.

Precision

In checking the method, several dust samples were collected from different localities; in each case the dust filter was divided exactly in two, and a known amount of standard beryllium solution added to one of the two halves. The two halves were then analysed separately for beryllium. Recoveries in all cases were between 90–105% at the 0.5 to 5 μg level. Below 0.5 μg the accuracy falls off, but the lower limit is estimated to be 0.1 μg, where there is an O.D. difference of 0.02 from the blank. (The blank on one particular batch of reagent does not vary more than ± 0.005 O.D.).

Use of method

At the time this paper was written, over 500 samples had been analysed, with beryllium contents ranging from <0.1 μg (over 50%) up to 20 μg. Only a very small minority (less than 3%) have been outside the tolerance level laid down; and with one exception these have all been surface samples.

Reagents

A. Complexing solution: Dissolve 8 g EDTA (disodium salt) and 2 g nitrilotriacetic acid in 80 ml water, adding ammonia dropwise to neutralise the free acid, and dilute to 100 ml.

B. Aluminon reagent: Aluminon is first purified as follows: Dissolve 2 g aluminon in 400 ml water and add 4 ml hydrochloric acid. Transfer to a separating funnel, add 500 ml ether and extract the aurine tricarboxylic acid. Filter the ether extract through a dry filter paper, and back extract the aluminon with 400 ml 0.5% ammonia. Run off the aqueous layer and dilute to 1 l.

Take 800 ml of this solution, add 200 g ammonium acetate and 20 ml acetic acid dissolved in 600 ml water. Add 1.2 g benzoic acid dissolved in 4 ml methanol, then add 400 ml 1% gelatin solution (polarographic grade). Adjust the pH to 5.8. Finally dilute to 2 l and store in a dark bottle.

C. Dilute ammonia 30%.

Air samples

Ignite the filter containing the dust sample at 800° until no carbon remains (if a membrane filter has been used, first ignite by applying a lighted match). Cool slightly, add about 0.25 g potassium bisulphate and fuse at about 600° for 1–2 min (the ash should yield a clear melt; if necessary add a little more $KHSO_4$). Cool, and extract the melt with 3 drops hydrochloric acid and about 3 ml water. If silica is present, centrifuge at this stage. Add from a polythene dropping bottle 10 drops of complexing solution, and dilute ammonia dropwise until the pH is in the range 4–7, (*Note a*) add 2 ml buffered aluminon solution and dilute to 10 ml in a graduated flask. Immerse the flask for 10 min in a boiling water bath, cool, and measure the absorption in a 4-cm cell at 5300 Å. This covers the range 0–8 μg Be. (*Note b*).

Note a

If there is an appreciable yellow coloration before adding the aluminon, due to iron, it is necessary to make a correction. To do this, measure the optical density of the final solution at 4200 Å and divide the figure by 30. Subtract this figure from the O.D. at 5300 Å to obtain the corrected beryllium reading.

Note b

If the reading indicates that more than 8 μg Be is present, take 5 ml of the final solution, add another 4 ml aluminon reagent, another 20 drops of complexing reagent, dilute to 25 ml and heat for a further 10 min; cool and measure as before. This extends the range to 25 μg Be, and if necessary a further dilution could be carried out in a similar manner.

Smear samples

These are treated in a similar manner to air samples but as they usually contain more total inorganic material, double the quantities of reagents used throughout and dilute the final solution to 20 ml.

Calibration

A calibration graph is prepared using the above procedure for air samples. A master standard beryllium solution is prepared by dissolving 0.1 g beryllium metal in 80 ml 20% hydrochloric acid under reflux and diluting to 100 ml. 1 ml of this solution is then diluted to 1000 ml to give a solution containing 1 μg beryllium per ml. Aliquots of

0, 0.5, 1, 2, 3, 4, 6 and 8 ml of this solution are taken to cover the range 0–8 µg Be. A separate calibration graph is required for smear samples over the range 0–16 µg Be. It is essential to prepare fresh calibration graphs for each batch of reagent.

Conclusion

This method can be regarded as a satisfactory alternative to the spectrographic method, in the determination of beryllium for monitoring purposes.

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SUMMARY

The requirements of beryllium monitoring are discussed. Emphasis is placed on developing an analytical procedure which is rapid, simple to operate, of adequate sensitivity and of reasonable accuracy. For air analysis, beryllium bearing dust is collected on a membrane filter, the beryllium is obtained in solution and determined spectrophotometrically, using aurine tricarboxylic acid (aluminon) as reagent. Interference due to other metals is avoided by the addition of suitable complexing agents. A sensitivity of 0.1 µg Be can be achieved.

RÉSUMÉ

L'auteur a mis au point une méthode de dosage du glucinium dans l'air et dans les poussières. Il s'agit d'une méthode spectrophotométrique, utilisant l'acide aurinetricarboxylique (aluminon) comme réactif.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Methode beschrieben zur Bestimmung von Beryllium in der Atmosphäre und in Staub. Als Reagenz dient Aurintricarbonsäure (Aluminon).

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POTENTIOMETRIC DETERMINATION OF MERCURY(II) WITH ETHYLENEDIAMINETETRAACETIC ACID

ANALYSIS OF BINARY MIXTURES

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REILLY AND PORTERFIELD[1] has shown that mercuric nitrate can be used for the coulometric backtitration of excess ethylenediaminetetraacetic acid (EDTA) in the determination of many metals. KHALIFA[2] *et al.* later showed that the Hg/HgY^{-2} system could be successfully applied for the same purpose. A silver amalgam electrode was immersed in a solution of the metal complexan which contained excess EDTA and was buffered to pH 8–11 with ammonium hydroxide and nitrate; a saturated calomel electrode and 0.05 M $Hg(NO_3)_2$ solution were used.

The cells and the potentials at the beginning of the titration and at 0.1 ml of titrant after the end-point may be represented as:

	pH	*8*	*9*	*10*	*11*
Hg/Hg^{-2} KNO_3 – KCl Hg_2Cl_2/Hg	mV	216	171	126	76
$Hg/[Hg(NH_3)_2]^{+2}$ KNO_3 – KCl Hg_2Cl_2/Hg	mV	326	286	240	191

This method permitted detection of the end-point with reasonable accuracy and several metals could be determined.

The aim of the present work was to develop a simple, rapid and accurate method for the determination of milli- and microgram amounts of mercury(II).

Comparatively little work has been done on the titrimetric determination of mercury with EDTA. (The gravimetric sulphide method is time-consuming and is not suitable for micro amounts of mercury.) Mercury(II) has been determined by direct titration with EDTA in presence of xylenol orange indicator[3], and indirectly with excess of EDTA and back-titration with magnesium or zinc solution in presence of Eriochrome Black T indicator[4].

A potentiometric procedure has the certain advantage that no interference with the colour change of the indicator occurs when mercury has to be determined in, for example, pharmaceutical products. A potentiometric method with potassium iodide as titrant and platinum amalgam as the indicator electrode[5] can be used to determine 0.5 to 70 mg of mercury. The present method permits the determination of 0.2 to 100 mg of mercury(II) with reasonable accuracy.

EXPERIMENTAL

Reagents

Twice-distilled water was used for all solutions. The materials were the most pure available. The metals were used generally in the form of their nitrates.

Solutions

Mercuric nitrate solution was prepared by dissolving 9.0577 g of the analytical grade reagent (Mallinckrodt) in 500 ml water with the addition of a minimum amount of conc. nitric acid (*ca.* 4 ml). The solution was standardised either gravimetrically as sulphide or volumetrically by back-titration of excess EDTA with a standard magnesium solution using Eriochrome Black T as indicator. Both methods gave the same result, *i.e.* 20.38 mg of mercury(II) per ml. Further dilutions were prepared from this stock solution.

EDTA solutions (0.05 to 0.005 *M*), were prepared and standardised in the usual manner.

Aluminium solution was prepared and standardised as previously described[6] from potassium aluminium sulphate. Other metallic solutions (except those mentioned below) were prepared in the usual way and standardised according to the procedures of SCHWARZENBACH[7]; the solutions were 0.01 to 0.03 *M* and all were made slightly acidic in nitric acid.

Manganous solution was prepared from AR manganous sulphate by dissolving 2.2306 g in water adding 2 ml of 9 *N* sulphuric acid solution and diluting to 500 ml with water. This solution was standardised according to FLASCHKA[8], excess EDTA being back-titrated with magnesium solution after addition of tartaric and ascorbic acids.

Zinc solution was prepared from AR zinc oxide by dissolving 0.8138 g in the minimum amount of 1 : 1 nitric acid and diluting to 500 ml with water; the solution was found to be 0.02005 *M*.

Buffer solutions (pH 8 to 11) were prepared and standardised as previously described. The pH values were checked with a hydrogen electrode. The titration apparatus and the potentiometer were essentially similar to those described previously[9].

PROCEDURES

Mercury alone was determined by titrating different volumes of buffered mercury solutions with EDTA solutions using the silver amalgam electrode to detect the end-points. Reverse titrations were also carried out.

The procedure for the analysis of binary mixtures of mercury and barium was based on the use of selective pH. Binary mixtures of mercury and aluminium were analysed with the help of masking agents such as triethanolamine or ammonium fluoride. Binary mixtures of mercury with any of the other cations mentioned were analysed by two potentiometric titrations; one gave the content of mercury and the other the content of mercury plus the other metal. In some cases mercury was masked with potassium iodide and the other cation was titrated with EDTA using a suitable buffer and indicator.

RESULTS

The molarity (0.1016) of the stock mercury solution was checked by titrating 2.5-, 5- and 7.5-ml portions of 0.04 *M* EDTA at pH values 8, 9 and 10; the inflexions near the end-point were 90–106 mV per 0.1 ml of titrant. When 1-, 2- and 3-ml portions of the same mercury solution were titrated with 0.04 *M* EDTA at pH 8 or 9, the inflection averaged 70 mV per 0.1 ml of titrant. The average molarity of the mercury solution from these titrations was 0.1016 which agrees well with the previous figure of 20.38 mg of mercury per ml.

The results obtained with 0.05, 0.02 and 0.01 *M* Hg or EDTA solutions are listed in Table I.

These results and some of the corresponding curves (Fig. 1) show that mercury

TABLE I

	Hg taken mg	*Hg found mg EDTA titrated with Hg*	*error %*	*Hg found mg Hg titrated with EDTA*	*error %*	*mV/0.1 ml Hg or EDTA*
A. 0.05 *M* Hg and EDTA						
pH 8	20.06	20.13	+0.36	20.01	−0.26	72
	30.09	30.19	+0.32	30.04	−0.20	71
	40.12	40.26	+0.36	40.07	−0.12	72
pH 9	20.06	20.16	+0.50	20.16	+0.50	85
	30.09	30.19	+0.32	30.19	+0.32	88
	40.12	40.26	+0.36	40.04	−0.20	86
pH 10	20.06	20.12	+0.30	20.06	0.00	93
	30.09	30.19	+0.32	30.04	−0.17	97
	40.12	40.26	+0.36	40.04	−0.20	94
B. 0.02 *M* Hg and EDTA						
pH 8	8.02	8.02	0.00	8.02	0.00	65
	12.04	12.07	+0.30	11.99	−0.35	60
	16.05	16.09	+0.24	15.97	−0.50	60
pH 9	8.02	8.05	+0.35	7.99	−0.45	77
	12.04	12.03	−0.03	12.08	+0.35	79
	16.05	16.02	−0.20	16.02	−0.20	75
pH 10	8.02	8.06	+0.50	8.05	+0.35	86
	12.04	12.08	+0.40	11.99	−0.35	85
	16.05	16.11	+0.40	16.02	−0.20	81
C. 0.01 *M* Hg and EDTA						
pH 8	4.01	4.03	+0.49	3.99	−0.49	55
	6.02	6.02	0.00	5.98	−0.70	52
	8.02	8.02	0.00	7.96	−0.80	51
pH 9	4.01	4.01	0.00	4.03	+0.49	60
	6.02	6.00	−0.30	5.99	−0.50	61
	8.02	8.00	−0.30	7.94	−1.00	60
pH 10	4.01	4.05	+1.00	4.05	+1.00	70
	6.02	6.06	+0.70	5.99	−0.50	71
	8.02	8.05	+0.30	7.94	−1.00	69

TABLE II

ANALYSIS OF MIXTURES OF MERCURY AND ALUMINIUM

Hg taken mg	*Hg found mg*	*error %*	*Al taken mg*	*Al found mg*	*error %*
A. 0.0434 *M* Hg + 0.1906 *M* Al with 0.02 *M* EDTA and 0.0434 *M* $Hg(NO_3)_2$ solutions.					
4.353	4.370	+0.39	2.573	2.568	−0.19
8.706	8.741	+0.42	5.146	5.158	+0.23
8.706	8.702	−0.05	2.573	2.576	+0.12
B. 0.0283 *M* Hg + 0.0382 *M* Al with 0.0202 *M* EDTA and 0.0283 *M* $Hg(NO_3)_2$ solutions.					
2.838	2.838	0.00	0.512	0.511	−0.19
5.677	5.469	−0.49	1.025	1.020	−0.49

(4 to 40 mg) can be determined with reasonable accuracy; reasonable potential jumps of from 50 to 97 mV per 0.1 ml of titrant are given at the end-point.

Below 0.01 M the results were about 2% low; better results were obtained below pH 9. At pH 8 and especially when smaller amounts of the buffer were used the error was less than 2%. It was found that buffer pH 6 (KH_2PO_4–NaOH) was best for the titration of 0.005 M mercury or 0.005 M EDTA in either direction. The results, which involved negligible errors, are shown in Fig. 2. It is possible to determine 200 μg of mercury(II) without difficulty.

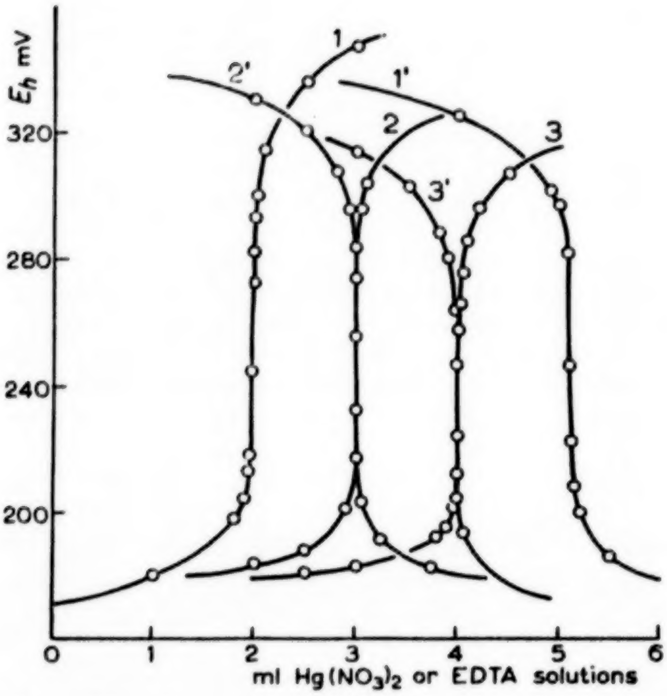

Fig. 1. Titration curves of EDTA against mercuric solution or vice versa, at pH 9. 1. 5 ml 0.04 M EDTA with 0.1016 M Hg solution. 1'. 2 ml 0.1016 M Hg with 0.04 M EDTA solution. 2. 3 ml 0.05 M EDTA with 0.05 M Hg solution. 2'. 3 ml 0.05 M Hg with 0.05 M EDTA solution. 3. 4 ml 0.02 M EDTA with 0.02 M Hg solution. 3'. 4 ml 0.02 M Hg with 0.02 M EDTA solution.

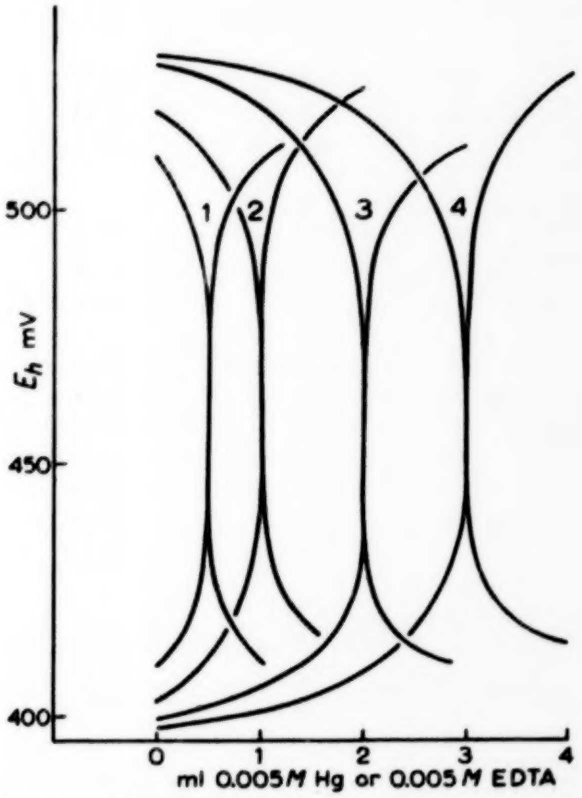

Fig. 2. Titration curves of EDTA against mercuric solution or vice versa. 1. 0.5 ml of 0.005 M Hg with 0.005 M EDTA or vice versa. 2. 1 ml of 0.005 M Hg with 0.005 M EDTA or vice versa. 3. 2 ml of 0.005 M Hg with 0.005 M EDTA or vice versa. 4. 3 ml of 0.005 M Hg with 0.005 M EDTA or vice versa.

Analysis of binary mixtures of mercury with some other metals by the use of masking agents[10]

Triethanolamine forms stable complexes with iron, aluminium and manganese. The aluminium couplex formed in ammoniacal solution serves to mask this metal. Fluoride forms stable complexes with aluminium, iron, titanium and beryllium and precipitates the alkaline earth metals. KHALIFA *et al.*[2] have studied the effect of triethanolamine, tartrate, citrate, sulphate and chloride on the titration of EDTA with mercury(II); they found that only appreciable amounts of chloride should be absent. Ammonium fluoride was examined as a masking agent in this investigation; buffered mercury or EDTA solutions were made 0.1 M in fluoride before titration. Fluoride ion had no effect over the whole range of pH except to improve the end-point inflection at pH 8 when EDTA was titrated with mercury. When the above-mentioned cations were masked by triethanolamine or ammonium fluoride, it was concluded that ammonium fluoride was preferable to triethanolamine. We also analysed mixtures of mercury and aluminium by adding excess EDTA and back-titrating with mercuric nitrate solution with and without fluoride present. In absence of fluoride, both metals were titrated and the aluminium was found by difference. Representative results are given in Table II.

Fluoride has also been used to mask lanthanum in the analysis of mixtures of mercury and lanthanum[11].

Analysis of mixtures of mercury and barium by means of selective pH[12]

Excess of EDTA was added and back-titrated at pH 8 (which gave the EDTA equivalent to mercury only) and at pH 10.5–11 (which gave both mercury and barium). Representative results are shown in Table III.

TABLE III

Analysis of 0.0504 *M* Hg + 0.05 *M* Ba

Hg taken mg	*Hg found* mg	*error* %	*Ba taken* mg	*Ba found* mg	*error* %
6.868	6.923	+0.81	5.056	5.075	+0.38
5.494	5.915	+0.45	10.112	10.120	+0.08
3.434	3.447	+0.38	5.056	5.051	−0.10

Analysis of binary mixtures of mercury with lead, manganese or zinc

Two methods were used. One involved the potentiometric titration of mercury in presence of the other cation with potassium iodide solution using silver amalgam as indicator electrode; both cations were then determined by potentiometric back-titration of excess EDTA with mercuric nitrate solution.

The other procedure involved the potentiometric titration of mercury(II) or the total content of the mixture as mentioned above; the other cation was then determined while mercury was masked with potassium iodide.

In the case of mercury and lead, lead was determined by adding a few crystals of tartaric acid, excess of potassium iodide (to form potassium mercuric iodide) and 30 ml of $NH_4OH - NH_4NO_3$ buffer pH 9, and titrating with 0.02 *M* EDTA using eriochrome black T as indicator. With mercury and zinc both the above methods gave satisfactory results in the presence or absence of potassium thiocyanate. When potassium thiocyanate (0.5 ml of 0.2 *M* solution per 1 ml of 0.01 *M* mercury(II) solution) was present equilibrium was attained only after 5 min near the end-point. The maximum inflection per 0.1 ml of 0.0101 *M* potassium iodide solution averaged 93 mV whereas it averaged 265 mV in the absence of thiocyanate. Such procedures can be used to analyse zinc mercuric thiocyanate. In the case of mercury and manganese, potassium iodide (0.5 ml of 0.1 *M* solution per 1 ml of 0.01 *M* Hg solution), ascorbic acid (0.2 ml of 0.1 *M* solution per 1 ml of 0.0268 *M* manganese(II) solution), tartaric acid and buffer pH 9 were added before titration of manganese(II) with EDTA solution; the sum of the metals was then determined by potentiometric back-titration

TABLE IV

Analysis of Hg (0.009 *M*) + Pb (0.010 *M*) or Mn (0.0268 *M*) or Zn (0.0201 *M*)

Volume ml	*ml 0.02 M EDTA*	*Molarity of metal*	*Molarity of Hg direct titration*	*mV per 0.1 ml 0.0101 M KI*	*Molarity of Hg back-titration*
4Hg + 2 Pb	0.990	0.00990	0.009027	267	0.00900
3Hg + 1 Pb	0.495	0.00990	0.009005	244	0.00903
2Hg + 3 Pb	1.490	0.00993	0.008960	293	0.00898
1Hg + 0.5 Pb	0.250	0.01000	0.008963	315	0.00895
4Hg + 2 Mn	2.680	0.02680	0.009019	206	0.00898
3Hg + 1 Mn	1.345	0.02690	0.009001	208	0.00899
2Hg + 3 Mn	4.020	0.02680	0.008989	300	0.00905
1Hg + 0.5 Mn	0.670	0.02680	0.008938	280	0.00904
4Hg + 2 Zn	2.010	0.02010	0.008950	70	0.00901
3Hg + 1 Zn	1.000	0.02000	0.009040	98	0.00901
2Hg + 3 Zn	3.020	0.02013	0.008950	99	0.00896
1Hg + 0.5 Zn	0.500	0.02000	0.009020	104	0.00888

of EDTA, the mercury being determined by difference. Representative results are listed in Table IV.

Analysis of binary mixtures of mercury(II) with nickel, cadmium or cobalt

Mercury(II) was titrated with potassium iodide and the total metals were determined by back-titration with mercuric nitrate, the other metal being determined by difference. Representative results are shown in Table V.

TABLE V

Analysis of Hg (0.010 *M*) + Ni (0.0201 *M*), Co (0.0200 *M*) or Cd (0.0201 *M*)

Hg taken mg	*Metal taken mg*	*Hg found by KI mg*	*error %*	*Metal found mg*	*error %*
8.024	2.359 Ni	8.088	+0.79	2.364 Ni	+0.21
6.018	1.180 Ni	6.028	+0.16	1.183 Ni	+0.17
4.012	3.538 Ni	3.999	—0.32	3.560 Ni	+0.62
2.006	0.590 Ni	1.996	—0.49	0.590 Ni	+0.00
8.024	4.496 Cd	8.053	+0.36	4.489 Cd	—0.15
6.018	2.248 Cd	6.047	+0.48	2.248 Cd	0.00
4.012	6.745 Cd	4.000	—0.30	6.740 Cd	—0.07
2.006	1.124 Cd	2.011	+0.25	1.124 Cd	0.00
8.024	2.369 Co	8.072	+0.59	2.369 Co	0.00
6.018	1.185 Co	6.054	+0.59	1.179 Co	—0.51
4.012	3.554 Co	3.992	—0.49	3.571 Co	+0.48
2.006	0.592 Co	2.011	+0.24	0.592 Co	0.00

The above data show that the procedure described is simple and suitable for the determination of many binary mixtures containing mercury(II). Furthermore, it can be modified for the analysis of mixtures of mercury with more than one cation.

SUMMARY

Potentiometric determination of mercury(II) with EDTA using silver amalgam as indicator electrode, is suitable for 200 μg to 100 mg of mercury. Binary mixtures of mercury(II) with several other metals can be analysed by different methods involving masking agents, selective pH and differential titrations.

RÉSUMÉ

Une méthode potentiométrique est proposée pour le dosage du mercure(II) au moyen de l'acide éthylènediaminotétracétique en présence d'amalgame d'argent comme électrode indicatrice. Des méthodes sont également proposées pour l'analyse de mélanges binaires du mercure(II) avec d'autres métaux.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur potentiometrischen Bestimmung von Quecksilber(II) mit Aethylendiaminotetraessigsäure und Silberamalgam als Referenzelektrode. Die Methode lässt sich auch zur Analyse binärer Gemische von Quecksilber(II) mit anderen Metallen verwenden.

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RAPID METHOD FOR THE DETERMINATION OF FLUORIDE IN LIQUIDS

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DISCUSSION

The determination of fluoride always presents a problem in sample handling. Standard ashing procedures depend on the volatilization of the fluoride. This is because it easily forms the volatile compounds HF and SiF_4. This property has, of course, provided the base for many successful separation procedures. Techniques involving the use of bombs have also been used successfully. At best, however, these procedures are tedious, time-consuming and require close attention. Also, a serious limitation of bomb techniques is that the sample size is limited. For trace fluoride determination (less than 100 p.p.m.) this is a severe handicap.

Other procedures which have recently been applied successfully to this analysis include the Shöniger flask technique[1] and the use of the Wickbold oxy-hydrogen burner[2-4].

The Shöniger flask technique had the appeal of simplicity and high speed, but the small sample size restricts the lower limit of fluorine determinable. The Wickbold burner[2,3] has been successfully used for the determination of halides and sulfur in liquids and gases, and a modification[4] of the Wickbold burner has been made to enable solids samples to be analyzed. But again the sample size is limited by the capacity of the combustion boat used to contain the sample during the decomposition stage.

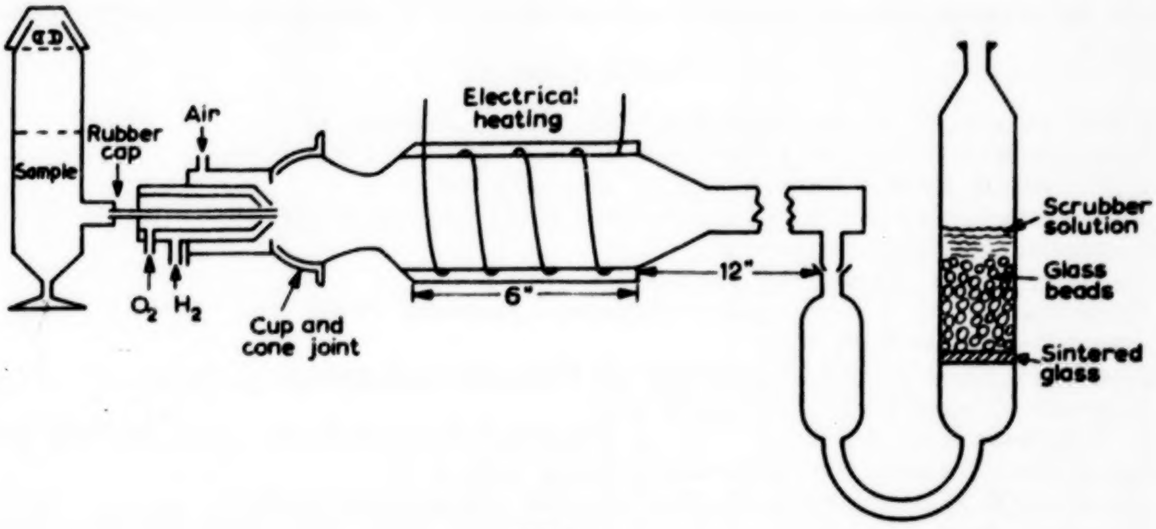
G.D
Rubber cap
Sample
Air
O_2
H_2
Cup and cone joint
Electrical heating
6"
12"
Scrubber solution
Glass beads
Sintered glass

Fig. 1.

The present procedure eliminates the problem of sample size to a considerable degree. Any amount of sample can be burned; also, the separation step is simple, rapid, and requires the minimum of attention.

Apparatus

Furnace. The furnace (Fig. 1) is made of Vicor. It is fitted with a glass 35/25 male ball joint at one end for attaching the burner, and a male joint at the other end to attach the scrubber.

The first portion of the tube is electrically heated to act as an igniter for the flame. This portion of the furnace is somewhat wider than the rest of the tube to allow for expansion of the hot, combusting gas.

Scrubber. The scrubber is a standard sintered glass scrubber with glass beads added to give better contacting between scrubber solution and combustion products.

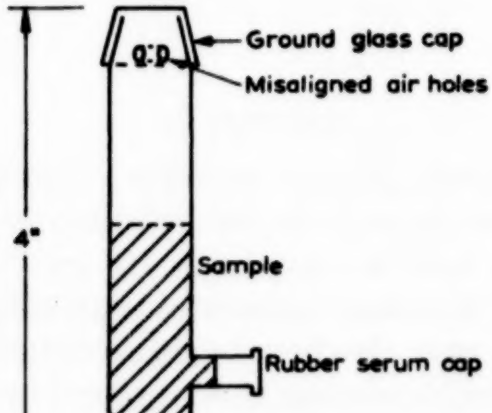
G.D
Ground glass cap
Misaligned air holes
4"
Sample
Rubber serum cap

Fig. 2.

Sample container (Fig. 2) This is a glass tube fitted with an open-end side-arm near the base. A rubber serum cap is placed over this side arm. A ground glass cap is placed on top. A small hole is drilled in the cap, and a similar hole is drilled through the container. When sample is being run, these holes are made to coincide by turning the cap to allow air to pass. At other times, the holes do not coincide. This prevents loss of sample by evaporation.

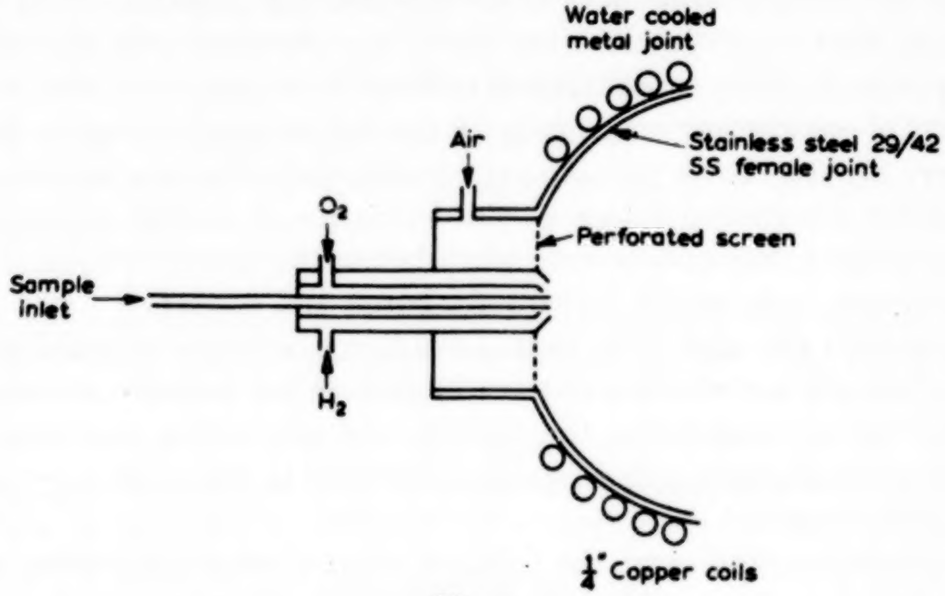

Fig. 3.

Burner (Fig. 3). The burner consists of a Beckman oxy-hydrogen burner brazed into a standard 35/25 stainless steel female joint. Space is left for a current of air. The burner is water-cooled to prevent overheating.

PROCEDURE

Igniting furnace

The furnace is heated up to red heat (600°). Oxygen pressure is raised to 3–5 psig in the burner. Hydrogen pressure is increased to 0.5 psig. Under these conditions, immediate ignition should take place. If it fails to ignite, shut off the hydrogen, then the oxygen, increase the furnace temperature and repeat the operation.

After ignition, the electrical heating should be turned off to prevent overheating the glassware. The oxygen and hydrogen pressures are adjusted to 10 and 1.5 psig, respectively. An air flow of 10–15 l/min is satisfactory.

Sample burning

The sample is poured into the sample container and weighed. After the furnace is ignited, the container is then attached to the burner by piercing the serum cap with the burner inlet capillary (Fig. 1). The air inlet holes in the cap are lined up to allow free flow of the sample. Control of feed rate is maintained by misaligning these holes. This control can be exercised during combustion of sample if necessary.

When sufficient sample has been burned, the sample container is removed and reweighed, the inlet holes being closed. The weight of sample burned is the difference in weight between the container and liquid before and after burning. For samples containing 100 p.p.m. F, 15 g is adequate.

Fluoride determination

The fluoride in the scrubber may be determined by any conventional method. The thorium nitrate procedure was used for the work reported in this paper[5]. Attempts to use the polarographic procedure[6] required excessive attention. This was presumably because any error in determining the complexed iron gives a six-fold increase in error for the fluoride analysis.

Use of 3-amino-methyl alizarin N-N-diacetic acid

Some preliminary studies were made on the use of 3-amino-methyl alizarin N-N-diacetic acid[7] as a colorimetric method for determining fluoride.

It was found that a good calibration curve was obtained over the concentration range 0–10 p.p.m. F. With concentration of fluoride greater than this, the color was bleached out. This concentration range is too limited for applications in the petroleum industry where the fluoride level can vary considerably. Further studies also showed that many metals interferred with the color formation if present in concentrations of 100 p.p.m. or greater. No studies were made below this concentration. These metals included aluminum, iron, nickel, vanadium, boron and copper.

It is believed that the color body in this reaction is a fluoro–cerium-organic addend complex, the formula for which is not yet known. Other metals can interfere in two possible ways: (*a*) by complexing the fluoride and preventing the formation of the color body, or (*b*) by forming a more stable color body in which the cerium is replaced by the interfering metal.

Spectrophotometric studies of the solution formed when interfering metals were present revealed that the wavelength of absorption shifted to the near IR or UV. This suggested that the metals were interfering by mechanism (*b*) and that the metal complex was not destroyed but modified.

Based on this observation, it seems possible that a metal producing a more stable metal fluoro–organo complex than cerium could be used for this reagent. Such a reagent would naturally be less troubled by metal interferences. Although the procedure would of necessity be instrumental, and therefore not applicable to visual qualitative analysis, it would still find a wide application in quantitative analysis.

Unfortunately, the present reagent is troubled by metal interferences, and since these metals are not eliminated in the combustion step, it was decided that this reagent was not generally suitable for application to petroleum fractions, except where the fluoride level and the metal concentrations are very low.

RESULTS

The results obtained using the combustion technique described and normal thorium nitrate finishing technique indicated that the method was rapid (20 min per analysis) and reasonably precise. Accurate results were obtained by burning two compounds which are normally difficult to decompose. Results are listed in Table I.

TABLE I

Compound	*Fluoride*		*% Recovery*
	Added (mg)	*Recovered (mg)*	
Pentafluoropropyl alcohol	18.4	16.4	89
	26.1	22.3	86
Hexafluorodichlorocyclopentane	39.8	37.8	95
	26.4	25.6	97
	27.8	26.4	97
	26.2	24.9	95
	29.8	27.5	93
	6.1	5.8	95
	5.4	5.1	95
	7.7	7.1	92

These results indicated that the type of fluorine analyzed affected the efficiency of decomposition. Most fluoro compounds are easier to decompose than these and presumably in these cases the per cent recovery would be improved.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Miss D. WEBB who carried out much of the experimental work, and to Esso Standard Oil Company for permission to publish this paper.

SUMMARY

A rapid procedure has been developed for the determination of total fluoride in liquids. The samples are burned in a modified BECKMAN oxy-hydrogen burner. The fluoride is scrubbed out of the products of combustion and determined in any conventional manner.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage des fluorures dans des liquides. On procède par combustion; on peut ensuite appliquer l'un des méthodes habituelles pour le dosage du fluorure.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur raschen Bestimmung von Fluoriden in Flüssigkeiten. Die Substanz wird in einer Sauerstoff-Wasserstofflamme verbrannt und das Fluor nach einer der bekannten Methoden bestimmt.

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CONTROLLED POTENTIAL ELECTROLYTIC DETERMINATION OF COPPER IN LEAD AND TIN-BASE ALLOYS

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Copper determinations in lead and tin-base alloys can be carried out by electrolytic, iodometric or photometric methods. Generally, these methods require the preliminary separation of copper as sulphide[1], or by salicylaldoxime[2], or the separation of tin and antimony as oxides[3]. More often tin and antimony are volatilized as bromides, lead is separated as sulphate, and then the copper is determined by constant current electrolysis[4]. In the case of tin-base alloys, the electrolysis can be carried out directly after dissolution in nitric–hydrofluoric acid, but the method has some limitations[4,5].

The two methods described here allow the determination of copper directly from the acid-dissolved alloy by controlled potential electrolysis; this advantageous analytical technique is excellently described by LINGANE[6] who also gives a complete bibliography. In lead–base alloys with a high percentage of antimony, double electrolysis may be necessary.

In tin–base alloys also, the lead may be determined along with the copper; for these alloys, the method is similar to another described previously[7] which was derived from LINGANE's method[6,8]. Here, it is extended to a 5-g sample in order to determine the lead (often present in small amounts) up to a percentage of 0.2%. For lead–base alloys the analysis is also carried out on a 5-g sample because the percentage of copper is generally low. Percentages lower than 0.2% can be better evaluated by photometric or spectrographic methods.

Reagents

Concentrated hydrochloric acid ($d = 1.18$). Concentrated nitric acid ($d = 1.38$). Concentrated ammonia ($d = 0.88$).

Nitro–fluoboric mixture: in a polythene bottle, saturate 40% hydrofluoric acid with boric acid, filter and dilute the filtrate with an equal volume of dilute HNO_3 (1 + 1); keep in a polythene bottle.

Wash solution: distilled water containing one drop of concentrated ammonia per liter.

I. LEAD–BASE ALLOYS

(1) *Antimony:* up to but not more than 1.5%.

Method of analysis

In a 400-ml beaker weigh 5 g of alloy in thin chips, add 20 g of tartaric acid, then 50 ml of distilled water and shake to dissolve the tartaric acid. Add 50 ml of the nitro–fluoboric mixture, cover with a watch glass and heat slightly until all the alloy has dissolved, except for a black residue consisting predominantly of copper which also remains in suspension in the form of flakes. Heat a little more; after a while the dissolution of the residue begins and nitrous vapours develop. The reaction is rather violent and the beaker should be removed from the heating plate to prevent overflowing of the liquid.

This rather violent reaction dissolves all the copper and, when it stops, all the alloy should be dissolved. However, if, on account of excessive heating, violent dissolution of copper starts before all the other metals are completely dissolved, some of the alloy may remain undissolved; if so, the solution should be heated moderately to obtain complete dissolution. In the meantime, however, some tin may precipitate and, in this case, the analysis must be started again from the beginning.

When the dissolution is complete, add, little by little, 4–5 g of urea and immediately wash the watch-glass and the beaker wall with some distilled water, then add 20 ml of 60% perchloric acid and dilute with distilled water. Allow to cool slightly, filter, if necessary, on double Whatman No. 41 paper, add 10 ml of 1% potassium permanganate solution, stir until the solution has discolored and dilute to 250–300 ml with distilled water.

Electrolyze at a cathode potential of —0.15 V *vs.* S.C.E. which, during the electrolysis, should be altered gradually to —0.20 V *vs.* S.C.E. Electrolysis takes from 30 to

45 min. When it is complete, wash the calomel electrode, the cathode and the anode with the washing solution; then wash the cathode with alcohol and ether, dry and weigh.

Silver and bismuth which may be present, co-deposit with copper and must be determined separately. Some lead dioxide deposits at the anode during the electrolysis.

The electrodes used were cylindrical, of the gauze type, with a height of 50 mm and a diameter of 35 mm (anode) or 53 mm (cathode); stirring was magnetic.

Alloys analyzed and results obtained

The preparation of synthetic solutions of lead-base alloys by dissolving weighed amounts of the pure metals, according to the method, proved impossible: tin precipitated before all the copper was dissolved.

Therefore four synthetic alloys — 1000 g of each — were prepared by smelting carefully weighed amounts of the pure metals in a graphite crucible heated in an electric furnace. The lead was fused first and then the copper in wire form was added; tin and the other metals were then added. The smelted alloy was protected by a layer of graphite and then poured into small ingot moulds of steel; the surface layer was removed before the chips to be analyzed were shaved off.

TABLE I

PERCENTAGE COMPOSITION OF THE ANALYZED ALLOYS

Alloy	*Pb*	*Sn*	*Cu*	*Bi*	*Sb*	*Zn*	*Ni*	*Fe*	*Cd*	*As*
1	70	27	1	—	1	1	—	—	—	—
2	55	41	1	—	1	2	—	—	—	—
3	71	24	0.5	0.5	1.5	0.4	0.1	2	—	—
4	68.95	28.75	0.3	—	1.5	0.1	0.1	0.1	0.1	0.1
5	bal.	8.85	0.26	tr.	4.18	tr.	—	tr.	tr.	tr.
6	40.99	44.00	4.91	—	10.13	—	—	—	—	—
177 A	bal.	4.64	0.33	0.03	12.04	0.08	—	0.06	—	0.06
53 C	bal.	5.16	0.214	0.093	10.20	—	0.0023	0.0017	—	0.044

Besides these synthetic alloys (designated as 1-2-3-4) two other alloys (Nos. 5 and 6) already analyzed by the ASTM methods[4], as well as the standards No. 177 white Metal A (British Chemical Standards) and No. 53 C (N.B.S.) were used in the tests. Table I shows the composition of these alloys.

The copper in alloys 1-2-3-4 was determined by the method proposed and satisfactory results (Table II) were obtained.

TABLE II

Alloy	*1*	*2*	*3*	*4*
Cu % (+ Bi %)	1.00	1.02	1.00	0.29
	0.99	1.03	1.02	0.32
	1.00	1.01	1.01	0.30
	0.99	1.03	1.01	0.30

In initial tests, perchloric acid and permanganate solution were not added but the rest of the procedure was identical to that described above. Under these conditions, copper took on a slightly dark appearance toward the end of the electrolysis, but the results (Table III) were just as good.

TABLE III

Alloy	*1*	*2*	*3*	*4*
Cu % (+ Bi %)	0.99	1.01	1.02	0.32
	1.02	1.04	1.01	0.30
	1.01	1.02	1.03	0.31
	1.00	1.03	1.02	0.31

(2) *Antimony:* more than 1.5%.

When the alloy contained more than 1.5% of antimony and copper was determined by the above method, after the almost complete deposition of copper (and bismuth) a co-deposition of antimony took place, whether perchloric acid was present or not.

In such cases, near the end of electrolysis it was advisable to accelerate co-deposition by rendering the cathodic potential more negative, so that the current intensity increased by 0.1–0.2 A. Electrolysis was stopped 5–10 min after the current had increased; in this way, it was certain that all the copper present had deposited.

In a tall-form 400-ml beaker, re-dissolve the deposit in 30 ml of dilute nitric acid (1 + 3) containing 5 g of tartaric acid, heat to 70°–80° and, while still hot, add 1 g of urea, dilute a little, add 3 g of succinic acid and 1 g of hydrazine dihydrochloride, adjust the solution to pH 4.5–5 with ammonia, filter if traces of platinum are present owing to the reduction with hydrazine, and finally, electrolyze at —0.45 V *vs.* S.C.E.[7].

By means of this double electrolysis satisfactory results (Table IV) were obtained.

TABLE IV

Alloy	*5*	*6*	*177 A*	*53 C*
Cu % (+ Bi %)	0.26	4.90	0.37	0.29
	0.26	4.93	0.37	0.30

(3) In presence of iron.

When 0.1 g of pure iron powder was added to the 5-g alloy sample and the solution was prepared for electrolysis by the above procedure without the addition of perchloric acid and permanganate, the co-deposition of antimony — even if present in high percentage — was avoided. However, copper either did not deposit completely (in which case it retained its normal appearance) or the last particles that deposited took on a dark color and then results were often high. In other words, the phenomena were similar to those observed[9] when copper is electrolyzed in the presence of high percentages of iron.

Table V shows how satisfactory results and poor results alternated with a high percentage of antimony in the presence of iron. If perchloric acid was present, antimony at high percentages co-deposited partially even when iron was present. Because of this unstable behaviour, no advantage was obtained by adding iron to the alloy being analyzed.

TABLE V

Sample	Cu % in alloys							
	1	*2*	*3*	*4*	*5*	*6*	*177 A*	*53 C*
a. 5 g of alloy + 0.1 g Fe	0.99	0.98	b	0.30	0.25	4.96	0.38	0.33
	0.99	1.00		0.29	0.26	5.07	0.34	0.29
	—	0.99		—	0.26	4.20	0.47	0.40
b. 4 g of alloy + 0.5 g Sb + 0.1 g Fe[a]	1.02	0.93	1.05	0.38				
	0.85	1.20	1.02	0.47				
	1.04	1.03	b	0.24				

[a] The percentages refer to a 4-g sample.
[b] 0.1 g of Fe was not added to this alloy because it already contained 2% iron.

II. TIN-BASE ALLOYS

Method of analysis

In a 400-ml tall-form beaker weigh 5 g of alloy and add 50 ml of hydrochloric acid (1 + 1). Cover with a watch glass and heat moderately to dissolve almost all the alloy: the residue left consists mainly of copper. At this point add, slowly and with caution, some concentrated nitric acid: oxidation of tin and antimony takes place at first, then copper starts dissolving. The reaction is rather violent and the beaker should be removed from the heating plate to prevent overflowing and excessive heating that might precipitate tin.

Once the violent reaction ceases, all the alloy should be dissolved; if not, heat moderately and, if necessary, add a little concentrated nitric acid. Any slight opalescence caused by tin may be eliminated with a little concentrated hydrochloric acid. Once the alloy is completely dissolved, wash the watch-glass and the beaker walls with a minimum of distilled water, heat slightly and add, little by little, up to 4-5 g of urea.

Next, add 10 g of tartaric acid, 2 g of succinic acid and 1 g of hydrazine dihydro-

TABLE VI

ANALYSIS OF TIN-BASE SYNTHETIC SOLUTION

All weights are in grams

Sn Weighed	*Sb Weighed*	*Cu*				*Pb*			
		Weighed	%	*Found*	%	*Weighed*	%	*Found*	%
4.3459	0.3198	0.1049	2.10	0.1047	2.09	0.1595	3.19	0.1596	3.19
4.2973	0.3236	0.2640	5.28	0.2639	5.28	0.0257	0.51	0.0250	0.50
4.3808	0.3216	0.1165	2.33	0.1162	2.32	0.2053	4.11	0.2064	4.15
4.4185	0.3304	0.2066	4.15	0.2063	4.15	0.0104	0.21	0.0106	0.21
4.3956	0.3302	0.2627	5.25	0.2630	5.26	0.0232	0.46	0.0224	0.45
4.3365	0.3295	0.0994	1.99	0.0988	1.98	0.0468	0.94	0.0470	0.94
4.3286	0.3194	0.2566	5.15	0.2573	5.15	0.0342	0.68	0.0338	0.68
4.3798	0.3250	0.1125	2.25	0.1120	2.24	0.0560	1.12	0.0568	1.14
4.3495	0.3164	0.1512	3.02	0.1506	3.01	0.0148	0.29	0.0150	0.30
4.2381	0.3176	0.2023	4.05	0.2015	4.03	0.1045	2.09	0.1047	2.09
4.3327	0.3132	0.1958	3.92	0.1961	3.92	0.2428	4.86	0.2415	4.83
4.3503	0.3083	0.3038	6.08	0.3038	6.08	0.1034	2.07	0.1028	2.06
4.3226	0.3112	0.1345	2.69	0.1352	2.70	0.0534	1.07	0.0520	1.04
4.4574	0.3262	0.1381	2.65	0.1387	2.68	0.0395	0.79	0.0385	0.77
4.3291	0.3104	0.1651	3.30	0.1649	3.30	0.0137	0.27	0.0134	0.27

chloride. Adjust the solution to pH 4.8 to 5.2 with ammonia; narrow-range pH test papers may be used, provided that the color of these papers at pH 4.8–5.2 has been checked with a pH-meter. Deposit the copper at —0.30 to —0.40 V *vs.* S.C.E.; then deposit lead on copper at —0.60 to —0.65 V *vs.* S.C.E. In both electrolyses, wait about 15 min after the current has dropped to a minimum constant value before washing and weighing the metals deposited on the cathode. Also in this case, silver and bismuth co-deposit with copper.

Results from synthetic solutions

The preparation of tin–base alloy synthetic solutions from pure metals presented no difficulty if lead was used as a very fine powder; otherwise the dissolution time was very long and tin precipitated.

Table VI shows the amounts of metals weighed and found, and the relevant percentages of copper and lead referred to an assumed initial alloy sample of 5 g.

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SUMMARY

In lead–base alloys, copper can be determined by a single controlled-potential electrolysis if less than 1.5% of antimony is present; otherwise, the deposit must be dissolved and re-electrolyzed. Iron tends to inhibit the co-deposition of antimony. In tin–base alloys, copper and lead can be determined successively. The sample weight is 5 g; percentages as low as 0.2% can be determined.

RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre dans des alliages à base de plomb, par électrolyse à potentiel contrôlé. On a pu doser ainsi des teneurs en cuivre allant jusqu'à une limite inférieure de 0.2%.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Kupfer in Bleilegierungen durch Elektrolyse mit kontrolliertem Potential. Bei einer Einwage von 5 g können noch 0.2% Cu erfasst werden.

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SEPARATIONS INVOLVING SULPHIDES

XII. SEPARATION OF THORIUM OR TITANIUM FROM SOME ELEMENTS THAT FORM THIOSALTS

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The present investigation deals with the separation of thorium or titanium from elements which can be estimated by decomposing their thiosalts with hydrochloric acid. The general method adopted was to treat the solution containing the two metals with sodium sulphide reagent and hydrochloric acid. The sulphide formed was then filtered and weighed, and thorium or titanium in the filtrate was determined as the oxinate or oxide respectively.

EXPERIMENTAL

Standard solutions of sodium arsenate, potassium antimony tartrate, potassium tellurite, selenious acid, ammonium molybdate, mercuric chloride, gold chloride, platinum chloride or potassium perrhenate and thorium sulphate or potassium titanyl oxalate were used.

Separation of arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from thorium

Measured volumes of the solutions were mixed and treated with 2 *N* sodium sulphide reagent in excess. A measured quantity of hydrochloric acid was added, the mixture was heated to boiling and allowed to cool to room temperature. The precipitate was filtered on a sintered glass crucible (porosity 4), washed and weighed as As_2S_5[1], Sb_2S_3[2], TeS_2[1], SeS_2[1], $MoS_3 \cdot 2H_2O$[3], HgS[4], Au_2S_3[2], $PtS_2 \cdot 3H_2O$[5] or Re_2S_7[4]. The following points should be noted:

1. If a precipitate appears on mixing the two solutions, it need not be dissolved.
2. For arsenic, platinum or rhenium the final acidity should be 6 *N*, for selenium 2 *N*, and for other elements 1 *N*.

The filtrate was then evaporated to about 50 ml to remove hydrogen sulphide, diluted to 250 ml and made barely acidic by addition of ammonium hydroxide. The solution was heated to about 70°, 2% oxine solution in 2 *N* acetic acid was added followed by 2 *N* ammonium hydroxide to precipitate the oxinate. The mixture was allowed to cool to 50° and the precipitate was filtered on a sintered glass crucible, washed with water, dried between 100°–110° and weighed as $Th(C_9H_6ON)_4, C_9H_7ON$[6].

30–38 mg of arsenic, 47–58 mg of antimony, 44–68 mg of tellurium, 33–60 mg of selenium, 32–40 mg of molybdenum, 68–85 mg of mercury, 9–23 mg of gold, 23–28 mg of platinum or 37–46 mg of rhenium were separated from 32–40 mg of thorium. The metals were recovered with an accuracy of:

As, —0.5% to + 0.25%; Sb, —0.19% to 0.0%; Te, 0.0%; Se, —0.37% to 0.0%; Mo, 0.0% to + 1.0%; Hg, —0.2% to + 0.25%; Au, 0.0%; Pt, —0.43% to + 0.27%; Re, —0.54% to 0.0%; Th, 0.0% to + 0.45%; Th, —0.15% to + 0.12%; Th, 0.0% to + 0.97%; Th, —0.24% to 0.0%; Th, —0.12% to + 0.97%; Th, 0.0% to + 0.45%; Th, —0.75% to + 0.36%; Th, —0.6% to + 0.48%; Th, ± 0.75%.

Separation of antimony, tellurium, selenium or mercury from titanium

Antimony, tellurium, selenium or mercury were determined as above as Sb_2S_3[2], TeS_2[1], SeS_2[1] or HgS[4] respectively. In the filtrate titanium was determined by precipitation with cupferron and ignition to TiO_2[7].

47–58 mg of antimony, 54–68 mg of tellurium, 33–41 mg of selenium, 68–85 mg of mercury were separated from 39–49 mg of titanium. The metals were recovered with an accuracy of:

Sb, 0.0% + 0.24%; Te, —0.19% to 0.0%; Se, 0.0%; Hg, —0.25% to 0.0%; Ti, —0.3% to 0.0%; Ti, —0.3% to 0.0%; Ti, 0.0% to + 0.6%; Ti, —0.24% to + 0.3%.

SUMMARY

Sodium sulphide can be used to separate arsenic, antimony, tellurium, selenium, molybdenum, mercury, gold, platinum or rhenium from thorium and antimony, tellurium, selenium or mercury from titanium.

RÉSUMÉ

Le sulfure de sodium a été utilisé pour la séparation de l'arsenic, de l'antimoine, du tellure, du sélénium, du molybdène, du mercure, de l'or, du platine ou du rhénium d'avec le thorium et également pour séparation de l'antimoine, du tellure, du sélénium ou du mercure d'avec le titane.

ZUSAMMENFASSUNG

Die Trennung von Arsen, Antimon, Tellur, Selen, Molybdän, Quecksilber, Gold, Platin oder Rhenium von Thorium und die von Antimon, Tellur, Selen oder Quecksilber von Titan kann mit 2 *N* Natriumsulfid erzielt werden.

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DIRECT DETERMINATION OF TRACES OF TOTAL OXYGEN IN NAPHTHAS

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Traces of oxygen in elementary and combined form in naphtha have become important in various petroleum-refining processes. Dissolved elemental oxygen causes fouling in heat exchangers[1]. Traces of water impair the activity of reformer catalysts[2]. Sometimes the undesirable constituent is carbon dioxide, carbon monoxide, or some other oxygenated compound. Although specific methods for each type of oxygen compound are available, there has been no satisfactory method of directly determining the total oxygen content of low-boiling petroleum distillates.

The direct determination of total oxygen in organic substances has been the subject of many recent papers[3–11]. Methods most widely used have been modifications of the SCHÜTZE method[9], in which the sample is pyrolyzed over carbon at about 1100°. The oxygen is quantitatively converted to carbon monoxide and, after oxidation to carbon dioxide, is determined manometrically[6], volumetrically[5], gravimetrically[4,8,9], or iodometrically[3,11]. However, these modifications are not accurate below 0.1% oxygen.

Nevertheless, the SCHÜTZE method could be used for determining trace amounts of oxygen in light hydrocarbons if the problems of sensitivity and volatility were overcome. To obtain a measurable amount of carbon dioxide, a large sample must be pyrolyzed. To prevent dangerous explosions, the pyrolysis rate must be carefully regulated. To minimize evaporation, during weighing and handling the sample must be enclosed in a container having relatively small openings. Provision must be made to purge atmospheric oxygen from the system after the sample is placed inside the pyrolysis tube. Finally, the sample container must remain inert at the pyrolysis temperature.

Fulfillment of these strict requirements was made possible by handling the sample in the magnetically controlled spiral shown in Fig. 1[7], rather than in a boat. Made of quartz, it is open at both ends and has a small quartz hook at one end. Evaporation during weighing and purging is minimized by the small open ends. The spiral can be completely filled without entrapping any air.

The spiral is manipulated by a bar magnet completely enclosed in quartz, with a hook on one end to engage the hook on the spiral. Spiral and manipulator can be controlled as a unit from the outside of the pyrolysis tube by an external magnet. Rotating the external magnet about the pyrolysis tube in the region of the manipulator rotates both it and the spiral. With each rotation, a small amount of sample is expelled from the end of the spiral.

With this sample-handling device, a satisfactory method has been developed for the trace determination of oxygen in naphtha. A modification[8] of the SCHÜTZE method was used as the basic procedure, although some changes were made in both the apparatus and operating procedure. In the apparatus: (a) a longer and larger pyrolysis tube was used to accommodate the spiral; (b) a larger furnace was necessary to give a longer heating zone; (c) a longer platinized-carbon filling was used to increase the life of the filling; (d) large granules of carbon were placed at the front of the platinized-carbon filling to smooth the flow of nitrogen; and (e) a removable roll of platinum gauze was placed in front of the carbon filling to collect pyrolytic carbon. In the operating procedure, the reverse purge was extended and appropriate changes were made to accommodate the use of the spiral.

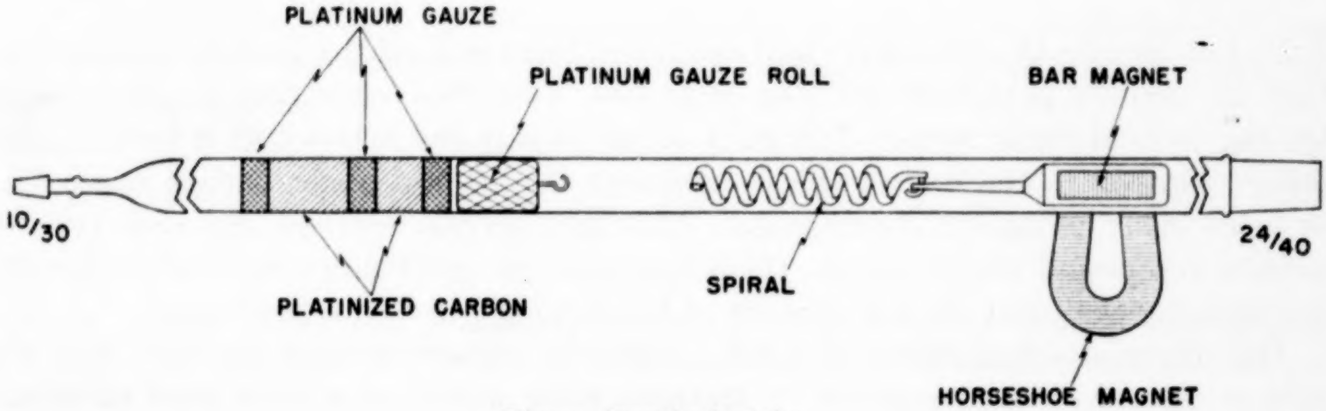

Fig. 1. Pyrolysis tube.

EXPERIMENTAL

Apparatus

Except for the pyrolysis tube, shown in Fig. 1, the rest of the train is as described previously[8]. The clear quartz pyrolysis tube is 20 mm in outside diameter and 70 cm long, with a Pyrex-to-quartz graded seal at each end.

The spiral is about 15 mm in diameter and made from 5 to 20 turns of quartz tubing 5 to 7 mm in outside diameter. As determined by the diameter and number of turns, the capacity ranges from 0.5 to 5 g of sample. Spirals of several sizes should be available.

The manipulator contains a bar magnet about 6 mm in diameter and 25 mm long. A horseshoe magnet is used as the external magnet.

The carbon filling is 10 cm long, retained at the ends and divided into two portions by 1-cm lengths of platinum gauze. A roll of platinum gauze 3 cm long is placed just before the front endplug to minimize deposition of pyrolytic carbon on the platinized carbon. The roll should be loose enough that it can be pulled out of the tube periodically to burn off the carbon.

Procedure

Sweep the apparatus with nitrogen for two hours at room temperature and then turn on all furnaces. Adjust the flow rate to 10 ml per min. After the pyrolysis-tube furnace is at 900°, continue purging the apparatus for at least four hours.

Weigh a spiral of appropriate size and fill it by connecting it to a small syringe and vertically drawing up the sample through the open end. There must be no enclosed air in the spiral. Weigh the sample to the nearest milligram.

Reverse the nitrogen flow and increase it to 30 ml per minute. Insert the spiral and the manipulator in the tube. Position the two units so that the spiral is about 4 inches from the furnace. Close the inlet joint and continue the reverse purge. To minimize volatilization of the sample, place a Dry Ice pack around the section of the pyrolysis tube containing the spiral. After 10 min of reverse purge, change to a forward flow, reduce it to 10 ml per min, and remove the Dry Ice pack. During the reverse purge, weigh the microabsorber on a microbalance.

Bring the spiral to about 1 inch from the furnace. Rotate the spiral and expell a emall amount of sample. If the deposited sample does not volatilize, move the spiral slightly closer to the furnace. Continue expelling small increments of sample as rapidly as possible without causing the entering flow of nitrogen through the flowmeter to fall below 2 ml per min. When rotation no longer expels any sample, carefully heat the pyrolysis tube with a low flame of a Bunsen burner, starting from a point 3 inches further from the furnace than the manipulator, and slowly moving the burner up to the furnace. Repeat the heating with a maximum flame.

After 40 min of sweeping with nitrogen, remove and weigh the micro-absorption tube.

Run a blank with an empty spiral which has been flushed with nitrogen. Utilize a reverse-purge for 15 min, and weigh the microabsorption during this period. Return the absorber to the train, change to a forward flow, and heat the tube with the maximum flame of a Bunsen burner. Sweep for 50 min and reweigh the microabsorption tube.

Calculate the per cent oxygen by the equation:

$$\% \text{ oxygen} = \frac{36.36(W_1 - W_2)}{W_3}$$

where W_1 is the weight of CO_2 from the sample, W_2 is the weight of CO_2 from the blank, and W_3 is the weight of sample.

After every 8 to 10 runs, the removable roll of platinum gauze should be taken out and the pyrolytic carbon should be burned off with a Bunsen burner. At this time, the carbon accumulated on the inside of the pyrolysis tube can be burned off by inserting a small quartz tube through the sample-inlet joint and introducing air against a reverse flow of nitrogen while the pyrolysis tube is heated with a Bunsen burner. To avoid high results after this burn-off, the pyrolysis tube can be reconditioned by passing hydrogen through it at 700° for 10 min. Hydrogen treatment is also helpful in conditioning fresh platinized carbon. Hydrogen is an excellent desorption gas and removes the adsorbed oxygen on the pyrolysis tube.

RESULTS AND DISCUSSION

To test the over-all efficiency of the train, highly oxygenated nonvolatile compounds were analyzed. To test the accuracy and precision of the method for trace determination of oxygen in naphtha, solutions containing known amounts of cetyl alcohol in iso-octane were prepared and analyzed. These test samples were interspersed with a wide variety of routine samples.

Analyses of highly oxygenated nonvolatile samples are shown in Table I. Because they were solid samples, a platinum boat was used in place of the spiral. The results obtained with these samples show that all of the oxygen is being converted to carbon monoxide and subsequently oxidized to carbon dioxide by the iodine pentoxide.

TABLE I

ANALYSES OF OXYGENATED COMPOUNDS

(Oxygen, weight %)

Sample	*Theory*	*Found* ($\overline{X} + s$)[a]
Cetyl alcohol	6.60	6.61 ± 0.10
Acetanilide	11.84	11.82 ± 0.14
Benzoic acid	26.20	25.97 ± 0.13

[a] Average of 3 determinations.

Good results were obtained even with benzoic acid, which is difficult to pyrolyze to carbon monoxide.

Analyses of synthetic samples prepared by adding known amounts of cetyl alcohol to iso-octane are shown in Table II. The iso-octane was purified by percolation through a 24-inch column of 8 to 200 mesh adsorption alumina. Aside from keeping the samples under a nitrogen blanket in the container and exercising the usual care

TABLE II

ANALYSES OF SOLUTIONS OF CETYL ALCOHOL IN ISO-OCTANE

(Oxygen, p.p.m.)

Calculated	*Found*				*Mean*	*Standard deviation*	*Average error*
125	149	129	126		135	9	10
144	169	142	159		157	14	14
202	173	219	236	209	209	26	22

in oxygen analysis, no special effort was made to exclude atmospheric oxygen or water vapor. In order to exclude completely atmospheric oxygen or water vapor, a very elaborate system of sampling, weighing, and sample insertion would be required. Even if such a system were used, the accuracy of the method may not be improved as the sample would be subjected to the oxygen-free atmosphere of such a system and might lose some dissolved oxygen or water vapor.

Air-saturated naphtha generally contains 30 to 80 p.p.m. of dissolved oxygen[1]; the calculated values for the synthetic samples include the average value of 51 p.p.m. oxygen found in the iso-octane. Standard deviations range from 9 to 26 p.p.m. oxygen, and the average error is about 10% cent of the oxygen present. Reasons for the positive error are not known.

TABLE III

ANALYSES OF LIGHT HYDROCARBONS

(Oxygen, p.p.m.)

Light naphtha A		43	65
Light naphtha B		83	112
Light naphtha C		123	134
Hydrodesulfurized naphtha D		14	30
Hydrodesulfurized naphtha E		23	34
Iso-octane, purified	44	53	57
Iso-octane, knock-testing grade			530
Alphamethylnaphthalene			648

Analyses of typical naphtha samples are shown in Table III. The values obtained for the light naphthas are typical of reformer feeds, which usually contain 20 to 50 p.p.m. of water. The deviations for duplicate values are about ± 20% from the mean. The hydrodesulfurized naphthas were run as soon as possible after they were taken from refinery units. The knock-testing iso-octane was purified by percolation through alumina and used to prepare the cetyl alcohol solutions in Table II.

Blank values range from 0.02 to 0.05 mg of oxygen (somewhat higher than the 0.007 mg reported earlier[8]). The high blank is probably due to the larger sample container and the larger pyrolysis tube, which offer more surface area for adsorbing air. However, with the 10 to 20-fold increase in sample size, precision remains high.

As an extension of the method, an attempt was made to determine trace oxygen in liquefied gases, such as butene. The sample was introduced from a glass bomb having a metal needle valve, which was connected to the stopcock near the sample-inlet joint. About 2 g of sample were bled into the system in one hour, and the oxygen determination was carried out in the usual way. Values of 680 and 86 p.p.m. total oxygen were obtained on two butene samples. Karl Fisher water values on the same samples were 520 and 40 p.p.m. oxygen, respectively. After six satisfactory runs, exceedingly high values were obtained. Apparently the butene was passing through the platinized carbon and being oxidized to carbon dioxide by the iodine pentoxide. Pyrolytic carbon was not formed on the platinum gauze but deposited on the platinized carbon itself, such that it became unreactive after six determinations. Thus, although the method is reliable for butene-type samples, frequent refilling of the pyrolysis tube is necessary if many are to be run.

SUMMARY

The low oxygen content and volatility of naphthas make existing methods for determining traces of oxygen and oxygen compounds in naphthas unreliable. The SCHÜTZE method has been modified to include a magnetically controlled spiral sample container from which a 5-g sample can be pyrolyzed safely by expelling it a few drops at a time. In the range of 100 to 200 p.p.m. oxygen, the standard deviation and the average error for synthetic samples are about 10% of the oxygen present. The deviation from the mean for routine samples containing less than 100 p.p.m. oxygen is about ± 20%.

RÉSUMÉ

L'auteur propose une modification de la méthode de SCHÜTZE, permettant le dosage de faibles quantités d'oxygène (combiné et libre) dans des fractions d'huiles minérales facilement volatiles.

ZUSAMMENFASSUNG

Es wird eine modifizierte Methode der Sauerstoffbestimmung nach SCHÜTZE beschrieben, die erlaubt, Spuren von Sauerstoff (frei oder gebunden) in leicht flüchtigen Erdölfraktionen zu bestimmen.

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A DINITROPHENYLATION METHOD FOR THE MICRO-DETERMINATION OF AMIDE NITROGEN

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INTRODUCTION

Amino acid analysis of cuticle-rich material from three samples of wool has shown that the cuticle is consistently poor in glutamic acid plus glutamine and aspartic acid plus asparagine[1]. It is therefore important to determine the amide-nitrogen content of both cuticle and whole fibre so that the amount of glutamic and aspartic acid present can be calculated. It seemed that this might be possible on a microscale by making use of the unwanted spot of 2,4-dinitroaniline ($DNPNH_2$), produced by reaction between 1-fluoro-2,4-dinitrobenzene (FDNB) and ammonia which is always present on the two dimensional paper chromatogram of the dinitrophenyl-amino acids. The problem of quantitative evolution of ammonia from the wool protein by hydrolysis in hydrochloric acid had been thoroughly investigated by LEACH AND PARKHILL[2]. However, LOCKHART[3] found only 50% reaction of FDNB with ammonia as compared with its quantitative reaction with a number of amines and this is paralleled by kinetic evidence on the reaction between 1-chloro-2,4-dinitrobenzene and these compounds[4].

This paper describes a satisfactory method for the analysis of amide-nitrogen of 0.5-mg samples of cuticle-rich material from wool.

EXPERIMENTAL AND RESULTS

Materials

Samples of Lincoln 36's and Corriedale 46's greasy wool were separated into base and tip and the grease removed as described previously[5]. A third sample of Lincoln 36's wool processed to top form was likewise cleaned and all samples conditioned at 65% R.H. and 20°. The 2 *N* HCl for hydrolysis was prepared by dilution of twice-distilled 6 *N* HCl with glass distilled water both freshly distilled. Acetone (A.R.) was refluxed with $KMnO_4$ and then fractionated to remove all traces of alcohols[6]. A sample of FDNB (British Drug Houses Ltd., Poole, Dorset) was fractionally distilled at 0.5–1.0 mm Hg-pressure at 116° to produce a light yellow product which was stored at 2°. Peroxide free diethyl ether (A.R.) was freed from quinones before use by extraction with 1% aq. NaOH (four times), dilute HCl (once) and distilled water (four times). Laboratory grade $DNPNH_2$ was not recrystallised since it was found to be chromatographically pure. Ammonium chloride, $KHCO_3$ and glycine were A.R. reagents used without further purification.

Preliminary experiments

The reaction between NH_3 and FDNB in aqueous solution at 40° by the method of LEVY[7], produced only 25% of $DNPNH_2$ even after 7 h heating. Reaction in a homogeneous solution of ethanol and 0.5 *M* $KHCO_3$ solution (2:1) according to

SANGER[8] gave much higher yields of DNPNH$_2$ but produced large quantities of ethyl 2,4-dinitrophenyl ether[4]. This compound, together with the DNPNH$_2$, was extracted by ether from the aqueous solution after dinitrophenylation and on a one-dimensional paper chromatogram ran just faster than DNPNH$_2$, but overlapped with it in a large range of solvents. It gave a colorless spot which showed up under U.V. light and gave a strong absorption at 345 mμ, the absorption maximum for DNPNH$_2$ in *N* HCl. To eliminate the interference of this material the reaction was repeated, ethanol being replaced by methanol, dioxan and acetone. With methanol, methyl 2,4-dinitrophenyl ether was produced which interfered in the chromatography, dioxan gave low yields but acetone appeared to be a satisfactory solvent. In order to increase the rate of reaction between NH$_3$ and FDNB the temperature of reaction was raised to 50° and a series of experiments carried out according to the following procedure.

An aqueous solution containing exactly 0.020 mg of A.R. NH$_4$Cl was evaporated to dryness, 1.0 ml 0.5 *M* KHCO$_3$ solution added by an automatic pipette followed by 1.5 ml acetone containing FDNB. After heating at 50° in a small stoppered flask for the appropriate time, 1 ml of a 5% solution of glycine was added and the heating continued for a further 30 min in order to remove all excess FDNB[3]. Five ml 0.5 *M* KHCO$_3$ was added, the solution extracted with ether (5×5 ml) and the combined ether extracts divided accurately into two parts. These were evaporated to dryness, the yellow residues dissolved in the minimum of acetone and applied as spots to Whatman No. 1 paper buffered with 0.1 *M* phthalate buffer at pH 5. The chromatograms were run in one dimension using 2-methylbutan-2-ol saturated with pH 5 phthalate buffer[9] for 16 h, and the spot due to DNPNH$_2$ identified by comparison with the pure DNPNH$_2$ run on the same paper. The paper was dried, the DNPNH$_2$ spot excised and its weight, together with that of three paper blanks, determined. The yellow colour was eluted with 5 ml *N* HCl at room temperature for 30 min and measured at its absorption maximum (345 mμ) in a 1-cm matched cell of the Unicam spectrophotometer. The small blank correction, about 0.01/100 mg of paper, was subtracted from the observed optical density. A further correction, amounting to 10–30% of the total observed optical density, was made for the amount of ammonia present in the reagents used. This correction varied in amount from one series of experiments to the next and was estimated by running one control experiment with each series. From the corrected value of the optical density the % yield of DNPNH$_2$ obtained from the NH$_4$Cl was calculated using the experimentally obtained value

TABLE I

YIELD OF DNPNH$_2$ FROM AMMONIA BY DINITROPHENYLATION

Weight FDNB *mg*	*Time of heating* *min*	*% Yield (mean of ≮ 2 determinations)*
5	180	65
10	180	72
20	180	82
30	180	78
20	20	69
20	45	80
20	90	72

of the molar extinction coefficient for pure DNPNH$_2$ in N HCl of $(1.43 \pm 0.027) \cdot 10^4$.

The results in Table I show the effect of variation of the amount of FDNB and time of heating on the yield of DNPNH$_2$. It is clear that about 20 mg of FDNB is required to give about 80% yield but there is no improvement on increasing the amount to 30 mg. Similarly 45 min reaction time gives about 80% yield but there is no advantage in increasing the time to 180 min. It therefore appears that the maximum yield obtainable is about 80% and it is interesting that the 20% loss of ammonia and/or DNPNH$_2$ during reaction and chromatography agrees very closely with the losses previously found in the dinitrophenylation of the amino acids[10]. In order to estimate possible losses of DNPNH$_2$ by further substitution of the primary amino group by dinitrophenyl groups and by extraction and chromatography, microamounts of DNPNH$_2$ were carried through the above procedure and the % recovery of DNPNH$_2$ on the chromatogram estimated. This amounted to 91.5% showing that there is a loss of 8.5% of DNPNH$_2$ in this way. It is unlikely that the additional loss of 11.5% of material is due to incomplete reaction between ammonia and FDNB since more stringent conditions of reaction do not increase the yield. It is possible that some ammonia could react with acetone[11] but this would still not explain the very similar results obtained in the dinitrophenylation of the amino acids[10].

For practical purposes the yield is constant at 80%, giving $\varepsilon = (1.14 \pm .036) \cdot 10^4$ as the mean of 10 experiments (excluding rows 1, 2 and 5 of Table I). This figure is used in all future experiments together with 20 mg FDNB and a heating period of 1 h at 50°.

Final procedure

A sample of cuticle-rich material, obtained as described previously[1] or whole fibre weighing about 0.5 mg was placed in a clean test tube, 3 ml 2 N HCl added and the tube closed with a spring-loaded ground glass stopper. The tube was heated at 100° for 2 h[2], after which time only a slight residue remained. An alternative technique of sealing the tube under vacuum and heating at 105° in the oven gave irreproducible results. The hydrochloric acid was evaporated at the water pump, 1.0 ml 0.5 M KHCO$_3$ added by an automatic pipette followed by a solution of 20 mg FDNB in 1.5 ml acetone. After heating at 50° for 1 h, 1 ml of 5% aqueous glycine was added and the heating continued for 30 min. Five ml 0.5 M KHCO$_3$ was added and the DNPNH$_2$ extracted from the aqueous solution with ether (5 × 5 ml). The ether extract was divided into two equal parts by volume, the ether evaporated at the

TABLE II

Amide nitrogen content of whole fibre and cuticle-rich material (moles/10^4 g material at 65% R.H. and 20°) with standard errors

Sample of wool	*Amide-N content of*		*Mean % cuticle material removed from the fibre*
	whole fibre	*cuticle-rich material*	
Lincoln 36's, virgin wool, tips removed	7.0 ± 0.2	7.2 ± 0.5	0.69
Lincoln 36's, processed to top form	7.4 ± 0.4	7.4 ± 0.6	0.56
Corriedale 46's, virgin wool, tips removed	7.3 ± 0.2	6.1 ± 0.1	0.50

pump and the yellow residue chromatographed as described above. The spots due to $DNPNH_2$ were excised, eluted with 5 ml N HCl for 30 min at room temperature and the optical density measured at 345 mμ. After correction was made for the paper blank and the amount of ammonia in the reagents as described above, the optical density was used to calculate the amide-N content of the protein material in moles/10^4 g material at 65% R.H. and 20°, using the value of the molar extinction coefficient of $1.14 \cdot 10^4$.

The figures for the amide nitrogen content of whole fibre and cuticle material recorded in Table II represent the means of at least four analyses.

In order to check whether the abrasive action of the descaler had any effect on the amide-nitrogen value the sample of Lincoln 36's virgin wool was rubbed back and forth across a very sharp abrasive edge until breakage occurred. Four analyses in which an average of 5.7% of material was abraded from the fibre gave a mean value of 7.6 ± 0.4 moles/10^4 g material at 65% R.H. and 20°. This is not significantly different from the whole fibre figure of 7.0 ± 0.2 hence showing that abrasion does not alter the amide-nitrogen content of the material.

DISCUSSION

From the results in Table II it is clear that the amide content of the cuticle-rich material is the same as that of the whole fibre for both samples of Lincoln 36's wool. However, this is not the case for the Corriedale 46's sample where the cuticle-rich material is significantly poorer in amide groups than the whole fibre. Differences in behaviour from one sample of wool to the next must therefore be expected. The more important use of these figures is in the calculation of the aspartic acid and glutamic acid content of the cuticle-rich material[12].

The results obtained for whole fibre analyses agree well with the value of 7.1 moles/10^4 g wool at 65% R.H. and 20° calculated from the results of LEACH AND PARKHILL[2] on Lincoln 36's wool. The mean standard error calculated over all sets of results is 4.5%. This figure is quite reasonable for such a determination which involves the use of extraction and paper chromatographic techniques and is to be compared with an overall mean standard error for amino acid determination of 6.9%[12]. The minimum amount of ammonia which can be estimated accurately by this method is about 2 μg. However if the amount of ammonia in the reagents could be reduced it should be possible to determine as little as 0.5 μg ammonia (40 μg wool) quite accurately.

ACKNOWLEDGEMENTS

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SUMMARY

A new micro-method is reported for the determination of amide nitrogen, based on the estimation of 2,4-dinitroaniline produced by the reaction between ammonia, quantitatively liberated from the protein, and 1-fluoro-2,4-dinitrobenzene. Application of the method to 0.5-mg samples of wool gives results in agreement with those obtained by other authors for the same type of wool. Analyses of cuticle-rich material obtained from these wool samples show that in one sample out of three the cuticle is significantly poorer in amide groups than the whole fibre. The mean standard error taken over all the analyses is 4.5%.

RÉSUMÉ

Une nouvelle méthode microchimique est proposée pour le dosage de l'azote des amides. Elle est basée sur une détermination de la dinitro-2,4-aniline, produite par la réaction entre l'ammoniac, quantitativement libéré de la protéine et le fluoro-1-dinitro-2,4-benzène.

ZUSAMMENFASSUNG

Es wird eine neue mikrochemische Methode beschrieben zur Bestimmung von Amid-Stickstoff. Das aus dem Protein in Freiheit gesetzte Ammoniak wird mit Fluoro-1-dinitro-2,4-benzol zur Reaktion gebracht und das entstandene Dinitro-2,4-anilin bestimmt.

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A SIMPLE SPECIFIC TEST FOR INNER-RING *o*-QUINONES

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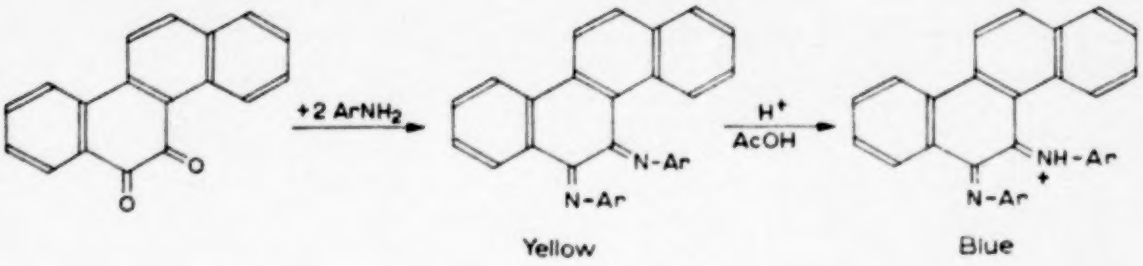
INTRODUCTION

In a previous paper[1] a thermochromic test for the detection of inner-ring *p*-quinones and fluorenones was described. This test gave positive results with the aromatic fraction of airborne particulates. With a modification of the procedure[2], benzofluorenes were detected in the air for the first time[3]. In another modified form the test has also been used to confirm the presence of anthracene in the air[3]. A test for terminal-ring *o*- and *p*-quinones has also been described recently[4]. Since a specific method for the detection of inner-ring *o*-quinones is not available in the literature, such a method has been developed.

The test procedure is based on the reported preparation of the bis-anils of chrysenequinone[5].

The following reaction probably contributes to some extent to the overall mechanism of color formation:



In line with this mechanism is the reversible decolorization of the blue color by alkali and the report by SINGH AND DUTT[5] that the brown bis-(*o*-methoxyanil) of 5,6-chrysenequinone has a wavelength maximum at 587 mμ (probably in acetic acid).

EXPERIMENTAL

Reagents and equipment

3,4-Dimethoxyaniline and 9,10-phenanthraquinone were obtained from the Aldrich Chemical Co., Milwaukee 12, Wisconsin. Dibenz[a,h]anthra-5,6-quinone was donated by Dr. VINCENT OLIVERIO. 5,6-Chrysene-quinone[5] and 9,10-retenequinone[6] were prepared by the oxidation of chrysene and retene, respectively.

A Cary Model 11 Recording Spectrophotometer was used for wavelength measurements.

Spot test procedure

To one drop of an acetic acid test solution in a 5-ml centrifuge tube add one drop of a 1.4% solution of 3,4-dimethoxyaniline in acetic acid. The mixture was heated on a water bath for 20 min. A blue to green color was formed in the presence of an inner-ring *o*-quinone.

Colorimetric procedure

To one ml of an acetic acid test solution in a 10-ml volumetric flask was added 1 ml of the reagent (1.4% 3,4-dimethoxyaniline in acetic acid). The mixture was heated on a water bath for 20 min, cooled and then diluted to the mark with acetic acid. A blank was run concurrently. The presence of inner-ring *o*-quinones was shown by the presence of a blue color and a wavelength maximum near 600 mμ. The results from the spot test and colorimetric procedures are shown in Table I.

TABLE I

3,4-DIMETHOXYANILINE TEST FOR INNER-RING *o*-QUINONES

Compound	*Colorimetric test*[a]		*Spot test identification limit, μg*
	λ_{max}	$\varepsilon \cdot 10^{-3}$	
9,10-Phenanthraquinone	590	16.5	12
9,10-Retenequinone	615	12.3	15
5,6-Chrysenequinone	615	12.3	5
Dibenz[a,h]anthra-5,6-quinone	590	17.1	18

[a] ε = molar extinction coefficient (concn. in gmoles/l).

DISCUSSION

Many aromatic amines were tried as the reagent in the test, but 3,4-dimethoxyaniline appears to be the best. A brilliant blue color was obtained with all the *o*-quinones in the colorimetric procedure (Table I). The identification limits in the spot test procedure ranged from 5 to 18 μg.

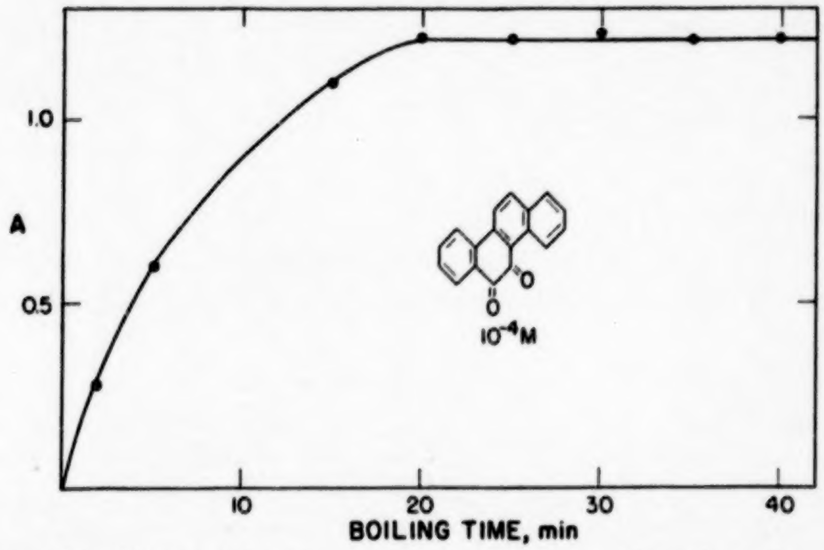


Fig. 1. Effect of time of boiling on absorbance at λ_{max} 615 mμ. Reaction of 5,6-chrysenequinone with 3,4-dimethoxyaniline by the standard colorimetric procedure.

The colorimetric procedure for 5,6-chrysenequinone was fully investigated. The reaction mixture had to be heated for at least 20 min at 100° for maximum color development (Fig. 1). The color was stable for at least 14 h. The volume of reagent was not critical. However, at least 1 ml was necessary for maximum color development (Fig. 2).

The following compounds gave negative results in the spot test procedure: benzil, chloranil, 1,4-naphthoquinone, 2,3-dichloro-1,4-naphthoquinone, 4-sulfo-1,2-naph-

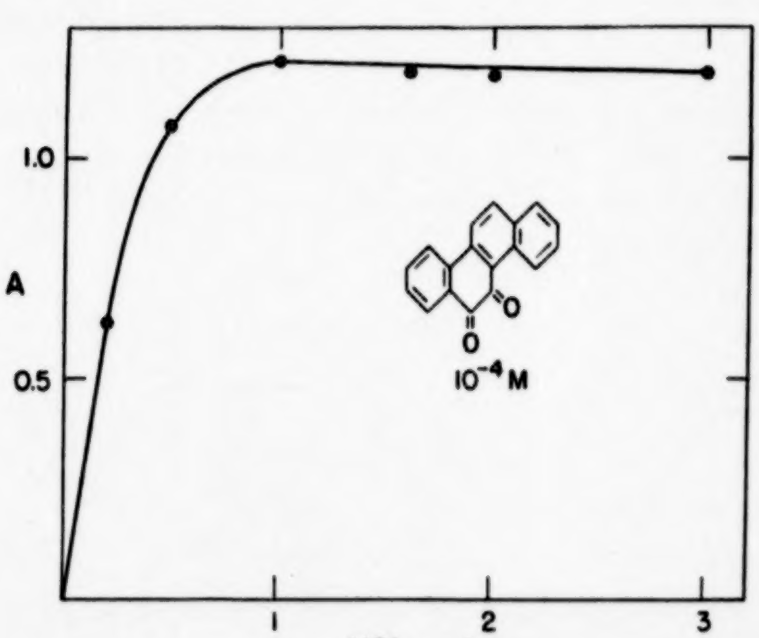


Fig. 2. Effect of volume of reagent (1.4% 3,4-dimethoxyaniline in acetic acid) on absorbance at 615 mμ. Reaction of 5,6-chrysenequinone with reagent by standard procedure.

thoquinone, fluorenone, acenaphthenequinone, anthraquinone and benzanthrone. The 1,4-naphthoquinones gave a scarlet color.

The presence of oxidants such as chromic acid could interfere in the color test, since a blue color, λ_{max} 585 mμ, is obtained immediately and without heat upon reaction of the oxidant with the reagent in the acetic acid. However, quinones should be easily separated from such an oxidant.

Another characteristic of the inner-ring *o*-quinones was the blue to green color they gave in sulfuric acid (Table II). The wavelength maxima of these solutions ranged from 585–670 mμ. The long wavelength band of the phenanthraquinones was approximately one-tenth the intensity of the analogous band of the other quinones.

TABLE II

COLORS, WAVELENGTH MAXIMA, MOLAR ABSORBANCES AND IDENTIFICATION LIMITS OF *o*-QUINONES IN SULFURIC ACID

Compound	*Color*	λ_{max}, mμ	$\varepsilon \cdot 10^{-3}$	*Identification limit*, μg
9,10-Phenanthraquinone	green	630	1.2	40
9,10-Retenequinone	green	670	1.7	16
5,6-Chrysenequinone	blue	585	12.5	3
Dibenz[a,h]anthra-5,6-quinone	green	655	10.5	5

Although this characteristic could prove of value in the characterization of the quinones, it must be emphasized that other types of compounds — quinonic and non-quinonic — give a blue to green color in sulfuric acid.

SUMMARY

A simple specific test for inner-ring *o*-quinones is introduced. The test consists of the reaction of the quinone with 3,4-dimethoxyaniline in hot acetic acid to give dye(s) absorbing near 600 mμ. Spot test and colorimetric modifications of the test are described. Other types of quinones and ketonic compounds give negative results. The spectra of the *o*-quinones in sulfuric acid are also presented.

With the new method, fairly specific tests are now available for (a) inner-ring *p*-quinones, (b) inner-ring *o*-quinones, and (c) terminal ring *o*- and *p*-quinones.

RÉSUMÉ

Une réaction simple et spécifique est proposée pour l'identification des *o*-quinones polycycliques. Elle consiste à faire réagir la quinone avec le diméthoxy-3,4-aniline.

ZUSAMMENFASSUNG

Als einfacher und spezifischer Nachweis polycyclische *o*-Chinone lässt sich deren Reaktion mit Dimethoxy-3,4-anilin verwenden.

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ON THE MIXED COMPLEXES OF TETRACYCLINE METAL CHELATES

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ISHIDATE AND SAKAGUCHI[1] and SAKAGUCHI AND TAGUCHI[2] have studied the tetracycline chelates and showed that only the phenolic β-diketone group in the molecule is responsible for chelate formation with metallic ions. Further investigations revealed that metal chelates of tetracyclines are always cationic chelates in which the molar ratio is 1 to 1.

It seemed likely that the metallic ion in this cationic chelate retains the ability to combine with other ligands. Consequently, tetracycline chelates should tend to combine further with chelating agents such as isoniazid, penicillin, etc. We have shown that several mixed complex compounds can be prepared; these may be termed multiligand or polyligand complexes. RITTER[3] and DALE AND BENNETT[4] obtained tetracycline–metal complexes with organic acids or penicillin–aluminium–sulfanilamide but no detailed information was given.

Isoniazid chelate (*INAH–chelate*)

FOYE AND DUVALL[5] have described INAH chelate. We have modified their procedure slightly. Copper–INAH chelate was obtained as blue crystals, its molar ratio being 1 to 1. Cobalt–INAH chelate was obtained as a light carmine-red crystalline powder with a 2 to 1 ratio of ligand to metal (Table I).

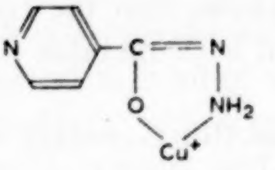
A fall in pH during metal chelate formation appeared in both cases (Table II). Since the pH decrease with cobalt chelates appeared above pH 7 but not below pH 7,

TABLE I

Complexes	*metal %*		*H_2O %*		*CT–HCl %*		*Formulae*
	found	*calc.*	*found*	*calc.*	*found*	*calc.*	
INAH–Cu(II)	20.7	24.1	0	0			INAH–Cu(NO_3)
INAH–Co(II)	12.9	12.34	3.5	3.78			$(INAH)_2$–Co$(NO_3)_2$–aq.
	14.4	12.90	11.6	11.8			$(INAH)_2$–$CoCl_2$–3aq.
INAH–Cu–CT	7.55	7.16	4.26	4.06	57.0	57.9	$(INAH)_2$–Cu–CT–HCl–2aq.
a	7.90	7.62	5.75	6.49	65.3b	58.6	INAH–Cu–CT–$HClO_4$–3aq.
INAH–Co–CT	7.79	7.73	6.57	7.07	65.9	68.2	INAH–Co–CT–HCl–3aq.
INAH–Fe^{+3}–CT	6.13	6.87	9.14	8.85	67.9	63.4	INAH–FeCl–CT–HCl–4aq.

a. Isolated at pH 4.0 b. As CT base

it seems likely that copper–INAH chelate has the structure (I) while cobalt–INAH has the equilibrium formulae shown as structures (II) and (III):



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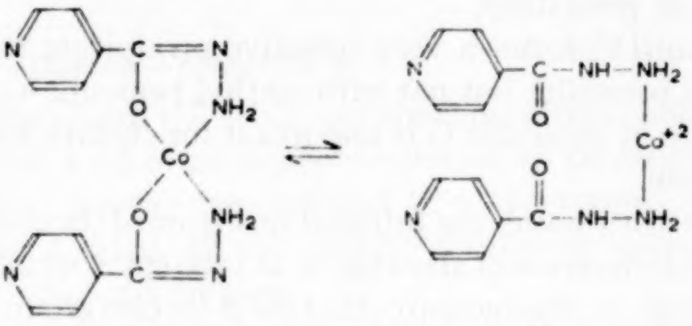


II

III

TABLE II

DECREASE IN pH IN FORMATION OF INAH CHELATES*

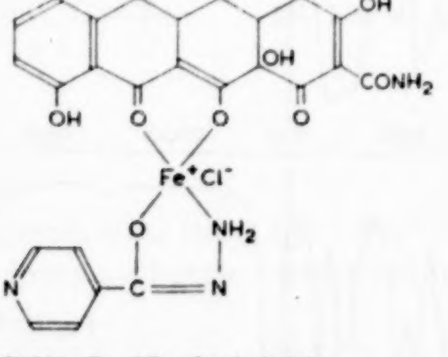
Metals	*pH*		*pH after mixing*	*Difference*
	Metal	*INAH*		
Cu(II)	2.79	2.79	2.68	−0.11
	4.30	4.34	3.88	−0.42
Co(II)	5.82	5.87	5.82	±0.00
	6.96	6.87	6.18	−0.69
CT–Cu(II)	2.97	2.79	2.92	+0.13
	5.11	5.03	4.44	−0.59

* Concentration of each solution was 1/200 *M*.

Mixed complex of chlorotetracycline metal with isoniazid

A mixed chelate of INAH–Metal–Chlorotetracycline (CT) was obtained by adding IHAH solution to an alcoholic solution of the chlorotetracycline–metal chelate. The mixed chelates formed were INAH–Fe–CT (brown precipitate) and INAH–Co–CT (orange powder) which were soluble in water and hot methanol, but insoluble in ether and chloroform. Both complexes had the molar ratio of 1:1:1 (Table I).

Only IHAH–Cu–CT (yellow-green precipitate) had a molar ratio of nearly 2:1:1 but it was slightly unstable on storage. In some of these cases a fall in pH drop occurred (Table II). The structure of the mixed chelate is postulated as follows:



INAH -Fe-CT mixed chelote

Isoniazid was destroyed by ferric iron without forming any chelates but a mixed chelate of INAH–Fe–CT could be obtained if previously prepared CT–Fe chelate was added to the INAH solution.

Penicillin chelates

Penicillin G forms precipitates with several metallic ions. Only copper(II) causes cleavage of penicillin[6].

Thorium(IV) forms a very sensitive precipitate from aqueous or methanolic solution with penicillin but not with methyl penicillin-G. This shows that the carboxylic acid group of penicillin G is important for chelate formation with metallic ions such as thorium.

On the other hand, the infrared spectrum of the cobalt–penicillin G chelate showed a remarkable decrease of absorbance at 1786 cm^{-1}, which was due to the β-lactam of penicillin G (Fig. 1); this indicates that the β-lactam group is essential for chelate formation.

TABLE III

Complexes	*Metal %*		*H_2O %*		*CT %*		*Formulae*
	found	*calc.*	*found*	*calc.*	*found*	*calc.*	
Pen. G–Th(IV)	27.33	28.70	6.41	6.67			PenG–$Th(NO_3)_3$–3aq.
Pen. G–Co(II)	7.86	7.74	4.46	4.74			$(PenG)_2$–Co–2aq.
Pen. G–Fe(III)	6.66	6.87	6.48	6.65			$(PenG)_2$–FeCl–3aq.
Pen. G–Th–CT	21.0	19.5	8.88	8.99	43.0	42.7	PenG–ThO–CT–HCl–6aq.
Pen. G–Th–DACT	22.3	21.00	8.29	8.14			PenG–ThO–DACT–5aq.
Pen. G–Fe^{+3}–CT	6.20	5.63	5.95	5.45	59.4	51.9	PenG–FeCl–CT–HCl–3aq.
Pen. G–Cu–CT	5.58		7.19		62.8*		at pH 6.0
Pen. G–Co–CT	5.83		4.67		67.3		at pH 6.0

* as CT base.

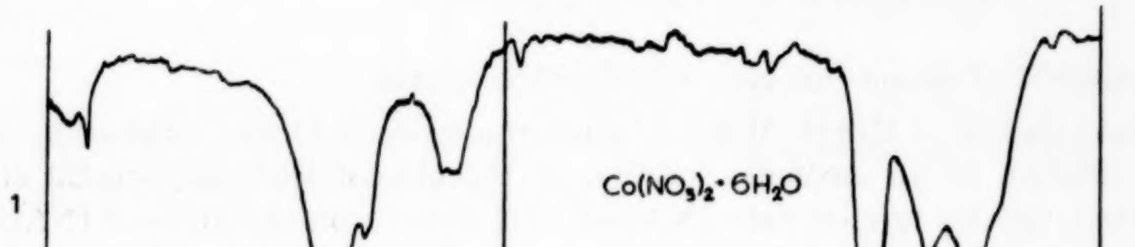


Fig. 1. Infrared spectrum of penicillin G–cobalt(II) chelate (2) compared with the components (1 and 3). In Nujol medium with sodium chloride prism.

Analysis showed that the thorium and cobalt penicillin G chelates have the molecular formulae Pen. G–$Th(NO_3)_3$–3aq. and $(Pen. G)_2$–Co–2aq. respectively (Table III).

Mixed chelate of chlorotetracycline–thorium–penicillin G

The Th–CT chelate was prepared from CT–HCl and thorium nitrate solution; it was dissolved in 2 ml of water and 1 ml of an aqueous solution of penicillin G was added gradually. An orange-yellow powder precipitated in a short time, and was washed with ethanol and ether and dried. It was slightly soluble in water but insoluble in methanol, ethanol, acetone, and dioxane.

Penicillin G forms a slightly soluble salt with chlorotetracycline (RUSKIN[7]). The fact that desdimethylaminochlorotetracycline (DACT) is able to form a chelate with thorium (Fig. 2) proves the existence of mixed complexes even in the CT–Th–Pen. G.

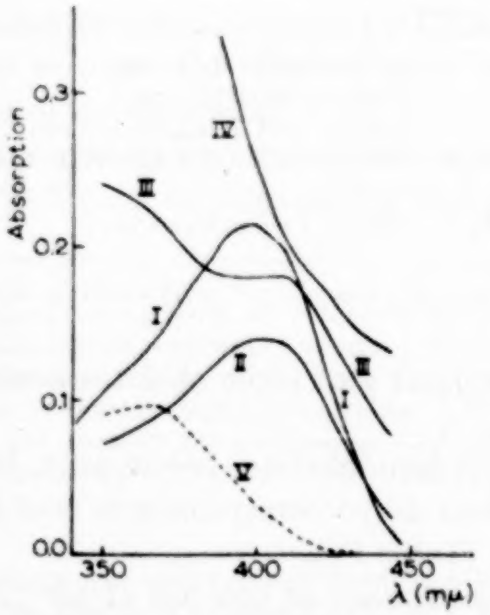


Fig. 2. Desdimethylaminochlorotetracycline (DACT) metal chelate. I. 10 μg/ml DACT–CH_3OH + Th(IV), II. 10 μg/ml DACT–CH_3OH + Zr(IV), III. 10 μg/ml DACT–CH_3OH + UO_2(II), IV. 10 μg/ml DACT–CH_3OH + Fe(III), V. 10 μg/ml DACT–CH_3OH + —.

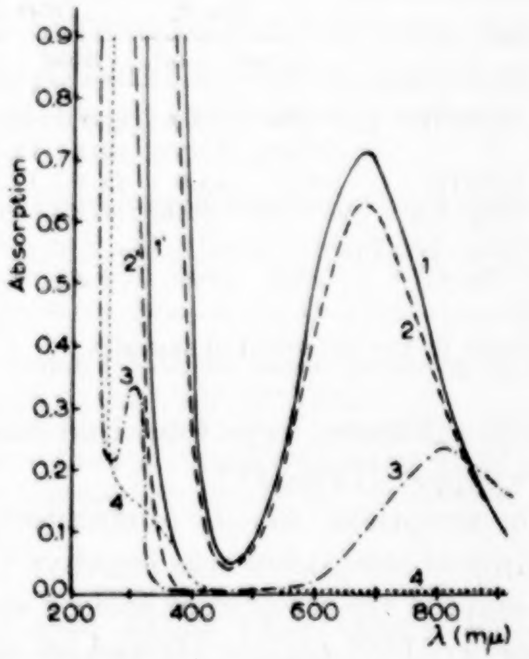


Fig. 3. Dihydrostreptomycin–Cu(II) complex and *d*-glucosamine–Cu(II) complex. 1. DST–Cu(II) 0.0125 *M*, pH 7.7, 1'. DST–Cu(II) 0.001 *M*, 2. Glu.–Cu(II) 0.0125 *M*, pH 7.2, 2' Glu.–Cu(II) 0.001 *M*, 3. $Cu(NO_3)$ 0.02, *M*, pH 3.5, 4. DST–$^3/_2$ H_2SO_4 0.1 *M*, pH 7.0.

DACT–thorium–penicillin G

Desdimethylaminochlorotetracycline (m.p. 157–160°) was prepared by the method of STEPHENS *et al.*[8]. It can form a chelate with thorium and other metallic ions in the same way as CT (Fig. 2).

Thorium–DACT was obtained by mixing DACT and thorium(IV) in methanolic solution; the potassium salt of penicillin G in methanolic solution (if it does not dissolve in pure methanol, a little water is added) was then added to form a precipitate which was dissolved in dimethylformamide. The solution was filtered and the metal chelate, DACT–Th–Pen. G, was precipitated by adding ether to the solution. The chelate could be purified by reprecipitation. The product was a yellowish powder which was insoluble in water and alcohol (Table III).

Dihydrostreptomycin chelate (DST–chelate)

FOYE *et al.*[9] reported on the streptomycin chelates of copper, cobalt and nickel. The chelates of dihydrostreptomycin and metal ions were also studied. The chelates were prepared by mixing dihydrostreptomycin solution with a slight excess of metallic ion solution; excess copper was removed by precipitation of the hydroxide by adjusting the pH of the solution to 7. Ethanol was then added to give a concentration of less than 40% of alcohol. In the case of copper, the precipitate obtained was deep blue (Table IV). This precipitate was soluble in water and 0.1 *N* potassium hydroxide, but insoluble in organic solvents. When the DST–chelate was prepared at pH 11, it was of a different type from that formed at pH 7; at pH 11 the chelates contained more copper (Table IV).

TABLE IV

Complexes	*Metal %*		*H_2O %*		*CT – HCl %*[a]		*Formulae assumed*	*pH*
	found	*calc.*	*found*	*calc.*	*found*	*calc.*		
DST–Cu(II)	7.66	7.67	5.9	6.39			DST–Cu$(HSO_4)_2$–3aq.	7
	18.03	17.50	14.4	14.5			DST–$(CuOH)_2$–7aq.	11
DST–Ni(II)	23.1	23.6	14.0	13.8			$[DST–(NiOH)_2]_2NiO$–22aq.	11
DST–Cu–CT	8.14	7.96	8.1	8.21	66.1	64.0	DST(CT–Cu–HCl)$_3$–SO_4–12aq.	6–7
DST–Th–CT[c]	26.3	26.6	6.4	6.25	54.8[b]	55.0	DST(CT–ThO)$_4$–13aq.	6–7

[a] percent to the dehydrated samples [b] calculated as a CT base [c] DST–HNO_3 was used

The streptidine moiety of streptomycin did not form chelates below pH 7, for the pH drop of streptidine was negative (Table V); but dihydrostreptomycin could form a chelate in the streptidine moiety above pH 11 (Table IV).

Copper–DST chelate showed an absorption maximum at 670 mμ at pH 7.7 and

TABLE V

DECREASE IN pH IN FORMATION OF METAL CHELATES

Ligands	*Metals*	*pH*		*pH after mixing*	*Difference*
		Metal	*Ligand*		
DST	Cu(II)	5.10	5.20	4.75	−0.35
	Ni(II)	6.30	6.30	6.10	−0.20
	Co(II)	6.25	6.30	6.20	−0.05
	Th(IV)	3.90	3.87	3.93	+0.03
Streptidine	Cu(II)	5.20	5.20	5.28	+0.08
	Ni(II)	6.30	6.30	6.25	−0.05
	Co(II)	5.70	5.70	6.00	+0.3
	Th(IV)	3.75	3.70	3.80	+0.05
Glucosamine	Cu(II)	5.40	5.40	4.80	−0.60
	Ni(II)	6.00	6.00	5.80	−0.20
	Co(II)	6.40	6.40	6.40	±0.00
	Th(IV)	3.75	3.85	3.80	—

copper–glucosamine chelate also showed a peak at 670 mμ at pH 7.2 (Fig. 3). The molar ratio of copper–glucosamine at 650 mμ is 1 to 1 and both showed marked pH decreases below pH 7 (Table V). Therefore, it may be assumed that dihydrostreptomycin combined with copper(II) at the N-methylglucosamine moiety in copper–DST chelate prepared at about pH 7.

Mixed chelates of DST-metal-CT

The affinity of copper for chlorotetracycline is larger than that for DST, and DST in the mixed chelate tends to separate on washing with ethanol and then water. Consequently, correct analytical values for the mixed chelate with DST could not be obtained. Qualitative tests for CT[2] or DST* showed that a mixed chelate must have been formed. The mixed chelate was prepared as follows. The copper–CT chelate was separated as mentioned above. A methanolic solution of this chelate was then added to an aqueous solution of DST to give a concentration of 40% methanol or less since 40% methanol did not cause any precipitation of DST. The solubility of copper–CT chelate in water decreases at pH 5–9. The mixed chelate could thus be separated by adding excess DST solution to the copper–CT solution, and adjusting the pH to 6–7. This chelate could be washed with water and ethanol without any danger of decomposing.

The preparation of mixed chelates suggests that enzyme processes may be clarified in the near future, for it is possible that enzyme functions are effected in mixed chelates.

SUMMARY

The mixed complexes of chlorotetracycline–metal chelates with isoniazid, penicillin G, and dihydrostreptomycin were examined with Th^{+4}, Cu^{+2}, Fe^{+3}, Co^{+2}, and Ni^{+2} ions.

A mechanism is proposed that accounts for the formation of the mixed complexes; cationic chelates of tetracycline have a molar ratio of 1 : 1 of metal to chlorotetracycline and mixed complexes are formed by combining with other ligands through the remaining covalencies. The properties and preparation of the mixed complexes are given.

RÉSUMÉ

Les auteurs ont effectué une étude sur les complexes et les chélates formés entre la chlorotétracycline, quelques cations (Co^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Th^{+4}) et les trois composés suivants: isoniazide, pénicilline G et dihydrostreptomycine.

ZUSAMMENFASSUNG

Es wird eine Untersuchung beschrieben über die Bildung und Eigenschaften der Komplexe, die aus Chlorotetracyclin-Metallchelaten, Co^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Th^{+4} mit Isoniazid, Penicillin G und Dihydrostreptomycin entstehen.

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* Sulfosalicylic acid–oxine–NaOH–NaOBr or diacetyl-β-naphthol reaction.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN TOBACCO SMOKE

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INTRODUCTION

This paper deals with the application of the recent improved method[1] for determining polycyclic aromatic hydrocarbons to tobacco smoke and also describes improvements in the apparatus and technique formerly used[2,3]. A very wide interest has been shown in the amounts of polycyclic aromatic hydrocarbons in tobacco smoke because of the known carcinogenic action of some of these compounds, and the present method has been developed to expedite the analysis as much as possible. Other developments are also discussed.

EXPERIMENTAL

Apparatus

The smoking apparatus is a development of that formerly described[3], and is shown in Fig. 1 which, apart from the suction device is drawn to scale. Interconnection between the various parts of the apparatus is standardised to allow rapid replacements and rearrangements and is made with B19 joints. All containers have B24 connectors. As far as possible standard equipment normally

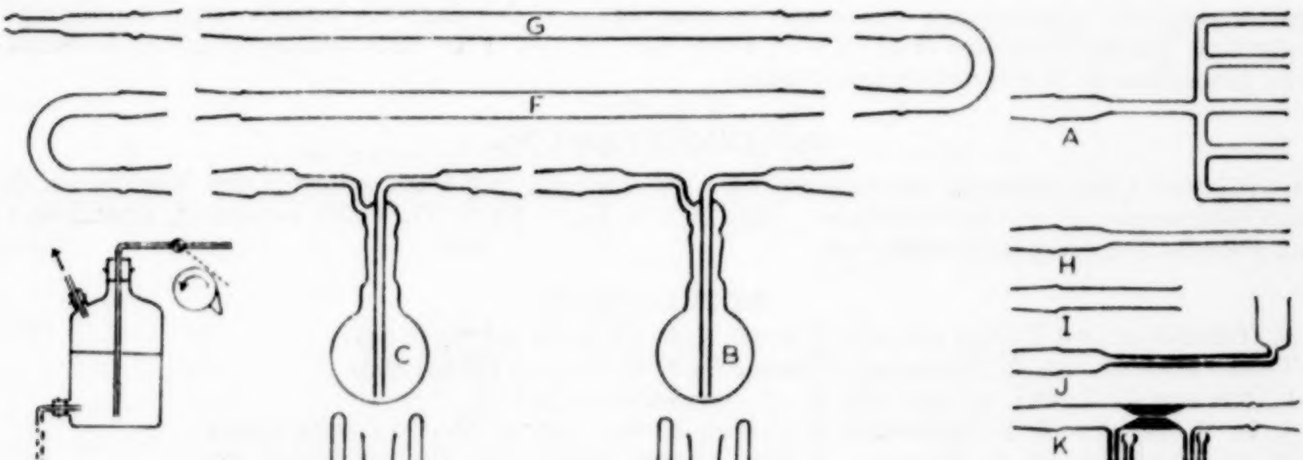

Fig. 1. The smoking apparatus.

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stocked by apparatus suppliers has been used. The collection flasks B, C, are used for solvents or can be replaced by cold traps D, E. The two colums F, G, filled with 3 mm glass balls, and used in conjunction with the flasks are capable of trapping all the smoke from five cigarettes simultaneously smoked without cold traps. All these parts are secured to a board with Terry clips. Multiple holders, A, to take five cigarettes were normally employed but larger ones have been used. However, smoking with holders taking more than ten cigarettes is difficult to control. Single cigarette holders H, cigar holders I, and pipes J, are all readily plugged in to this equipment, and ancillary equipment such as flowmeters K, thermometer or thermocouple ports L, and manometers M, can also be added. Suction pressures and times are controlled by the distance between the aspirator levels and the length of the cam used to open the stopcock. Although some workers prefer to use constant volume suction[4-6], it is especially convenient to use constant pressure suction for systems in which the interchange of various smoking and collecting devices may be needed. Once the conditions have been standardised by means of a flowmeter and manometer, this method of smoking is in all respects as satisfactory as any other.

Smoking and analytical technique for cigarettes

All materials and apparatus should be purified and cleaned as described previously[1].

The simplest technique for analysis of cigarette smoke is to use about 500 cigarettes; to smoke them in a multiple holder with spectroscopically pure cyclohexane in the flasks and with the timing and suction adjusted to suit the type of smoking habit it is desired to imitate. In Great Britain for normal size cigarettes (7 cm long and 0.8 cm diameter) the average type of smoking corresponds to puffs of 2 seconds duration with suction pressure equal to 25 cm of water. With these conditions smoking to a stub length of 1.5 cm requires a total smoking time of about 12 min.

The cyclohexane is poured off after the smoking is over and the whole apparatus (including the flasks) extracted with hot acetone. Cyclohexane soluble compounds are then removed from the acetone solution by the following process. The acetone solution is reduced to about 50 ml, mixed with an equal volume of cyclohexane, and the mixture distilled until the temperature of the vapour reaches 72°. It is then allowed to cool, the cyclohexane poured off from the semi solid residue and this is then repeatedly heated with several quantities of cyclohexane each of which is poured off in turn. All these solutions combined are worked up separately from the original cyclohexane solution as follows.

The cyclohexane solutions are shaken in turn three times with 2 *N* sulphuric acid, water, 2 *N* sodium hydroxide and finally again with water until the washings are neutral. The neutral cyclohexane solutions are dried with anhydrous calcium chloride and separately reduced to small volume (10 ml). Sometimes stubborn emulsions are formed during the washing processes but they can be broken by adding potassium chloride.

The solution in cyclohexane is placed on a large column of active alumina (10–12.5 cm) (Peter Spence, type H, 100 to 200 mesh), eluted with cyclohexane and collected in 3-ml fractions. Selected fractions throughout the sequence are examined in the D.K.2 U.V. recording spectrophotometer between 250 and 500 mμ. The fractions are diluted if necessary to give spectra with suitable absorption at the lower wavelengths. Generally about 200 fractions are collected. Automatic collection of fractions is preferable in order to ensure even distribution of components in the sequence. The object of examining the fractions in this preliminary chromatography is to select groups of fractions for combination in later chromatographic separations in order to segregate the compounds to be determined. The eluates in selected groups (generally two or three) of fractions are combined, distilled to small bulk (10 ml) in a water bath and rechromatographed on alumina columns of two activities (5 ml on each) to facilitate recognition of individual compounds in the chromatographic series. The alumina activities recommended are those formerly found suitable to space the compounds evenly in the sequence[1], that is in equilibrium with the vapour of either 50% or 70% sulphuric acid. These later columns are smaller and the size is best determined by a preliminary experiment. More complete separations can be effected by repeating the separations on additional small columns, but it should be noted that losses occur with each successive chromatographic process.

DISCUSSION

With tobacco smoke fractions a great deal of absorption is observed in the ultra-violet and most of this is due to other neutral compounds than the polycyclic aromatic hydrocarbons. This makes it necessary to use the "baseline" technique[1], for quantitative work. It is also important to complete the analysis as soon as possible because of possible losses of hydrocarbons during storage in solution.

Other investigators[6-12], have commented upon the difficulties of detecting and measuring amounts of these compounds totalling only to a few parts per million in the presence of other highly absorbing neutral components and have proposed and used various ways of overcoming the difficulties.

The most complete identifications were those of VAN DUUREN[7] who, commencing with 4 kg of smoke condensate (corresponding to 174,000 cigarettes), after chromatography on a large scale isolated the mixed picrates of the polycyclic aromatic hydrocarbons in impure form. TARBELL's paper chromatographic method[13] was used to isolate the pure hydrocarbons. The spots, recognised in ultra-violet light were cut out, redissolved, and identified by their ultra-violet spectra. The merit of the method is in the unmistakable identification of the complete spectra, but the yields were low and to an undefined extent so that it could in no sense be called quantitative. The length of the process and the large quantities required also make it impossibly tedious for repetitive and comparative work.

Even larger scale experiments of WRIGHT[14] have given pure products, and pure crystals of 3,4-benzpyrene and other hydrocarbons were first obtained from tobacco smoke in his laboratory. The smoking process corresponded more to pipe smoking than cigarette smoking and the yields were not quantitative. Crystalline samples of 3,4-benzpyrene have also been obtained by HOFFMAN[15] from cigarette smoke.

Fluorescence spectroscopy was employed to confirm the first determinations of 3,4-benzpyrene in tobacco smoke[16], and has since been used by several workers as a detecting and determining process. BENTLEY AND BURGAN[6] prefer fluorescence spectroscopy to ultra-violet methods for determinations, but HOFFMAN AND WYNDER[15] regard it solely as confirmatory of identity and not so accurate as U.V. spectroscopy for quantitative work because of quenching effects. LATARJET *et al.*[11] also use a sensitive fluorescence method for determinations. The variation in reported amounts of 3,4-benzpyrene (which is still the most potent carcinogen found in tobacco smoke) vary between about 1 to 18 micrograms in the mainstream smoke from 100 cigarettes. If one single investigation[10] is not included most determinations lie between 1 to 3 micrograms and, when variations of smoking method and analytical techniques are considered and also the possibility of losses during separation, this must be considered good agreement.

Of all the methods, the present, which employs the technique of elution chromatography with two activities of alumina, is most convenient and rapid, and is specially satisfactory for comparisons because it requires only a few hundred cigarettes for each determination.

ACKNOWLEDGEMENTS

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SUMMARY

Improvements have been described in the apparatus and methods employed in determining polycyclic aromatic hydrocarbons in tobacco smoke by alumina-column chromatography and automatic ultra-violet spectrophotometry.

RÉSUMÉ

Des perfectionnements ont été apportés à l'appareillage et aux méthodes utilisés pour le dosage des hydrocarbures aromatiques polycycliques dans la fumée de tabac.

ZUSAMMENFASSUNG

Es wird eine verbesserte Apparatur und Methode beschrieben zur Bestimmung polycyclischer aromatischer Kohlenwasserstoffe im Tabakrauch.

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THE DETERMINATION OF TANTALUM AND TUNGSTEN IN ROCKS AND METEORITES BY NEUTRON ACTIVATION ANALYSIS

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INTRODUCTION

In the past the determination of trace quantities of tantalum and tungsten in rocks and other materials with a complex matrix has been hampered by the lack of suitable analytical methods. While methods for the determination of these elements on the microgram scale are available, determinations at the sub-microgram level are difficult, particularly with tantalum where the utilisation of a chemical property in the final stage of the estimation frequently necessitates a separation from niobium.

RANKAMA[1], in his comprehensive study of the geochemistry of tantalum, avoided a separation from niobium by determining the element by X-ray spectrography after enrichment of the mixed earth acids by phenyl arsonic acid precipitation and separation from titanium by digestion with salicylic acid.

The abundance of tungsten in igneous rocks has been investigated by SANDELL[2]. Rock samples were dissolved in mixed acids and a double sodium hydroxide precipitation was used to remove iron and titanium. Molybdenum was precipitated with hydrogen sulphide and tungsten determined colorimetrically as the lower valency thiocyanate after ether extraction. Large quantities of vanadium interfere in the determination. More recently VINOGRADOV *et al.*[3] have published the results of a systematic investigation of the tungsten and molybdenum contents of various rocks using a spectrochemical method. Samples of the rock were fused with sodium carbonate and the melt extracted with water, acidified with hydrochloric acid and tungsten and molybdenum co-precipitated with tannin and methyl violet. The precipitate was separated, dried and ignited and tungsten and molybdenum determined spectrographically in separate portions of it.

A number of reviews of the technique of radioactivation analysis have been published[4,5] and the application of the method to materials of geochemical interest is exemplified by the work of CABELL AND SMALES[6]. Briefly the chief advantages of the technique lie in its freedom from blank difficulties and from contamination errors after irradiation and, since an inactive isotopic carrier is added before the sample is processed chemically, chemical separations at the microgram level are avoided.

The method of neutron activation analysis is insensitive to natural niobium and in consequence it is a particularly valuable technique for the determination of tantalum. KOHN[7] has described the direct determination of tantalum in ferro–niobium and niobium ores, and LONG[8], BEYDON AND FISHER[9] and EICHOLZ[10] have also described methods for the determination without chemical separation. A chemical separation for the mixed earth acids was used by MILNER AND SMALES[11] in the determination of niobium in stainless steel. Conventional steps were used to isolate the oxides from the steel and following irradiation together with tantalum pentoxide standards tantalum in the mixture was determined by gamma spectrometry.

BROOKSBANK, LEDDICOTTE AND REYNOLDS[12] have used neutron activation analysis to determine tungsten and other impurities in titanium, and tungsten has been determined in silicon by JAMES AND RICHARDS[13]. A method using a low level radium-beryllium neutron source has been described by HUARINGA[14] and LELIAERT *et al.*[15,16] have used low level neutron source in the determination of tungsten in high alloy steels both with and without chemical separation.

A more generally applicable method for the determination of tantalum and tungsten has now been developed and is described in this paper. The method has been applied to the analysis of some iron and steel standards, rocks from the Skaergaard Intrusion of East Greenland, the standard granite G1 and diabase W1 and some stony and iron meteorites.

NUCLEAR DATA

Table I contains a list of some nuclear characteristics of the nuclides produced by thermal neutron irradiation of tantalum and tungsten, and the activities induced in them by irradiation in the Harwell Pile (BEPO) for one month. The greatest sensitivity in the estimation is found with the nuclides ^{182}Ta and ^{187}W, and assuming

TABLE I

NUCLEAR DATA FOR TANTALUM AND TUNGSTEN

Target isotope	*Abundance in natural element (%)*	*Isotopic activation cross-section (barns)*	*Product on neutron activation*	*Radiation and energy (MeV)*	*Half-life*	*Activity d/m/μg after 7 days in BEPO*
$^{180}_{73}$Ta	0.012	—	^{181m}Ta	Isomeric transition	0.33 sec	—
			^{181}Ta	stable		
$^{181}_{73}$Ta	99.988	0.07	^{182m}Ta	Isomeric transition	16.5 min	$1.4\cdot10^4$
		22	^{182}Ta	β^- 0.514, 0.44, 0.36 γ 1.22, 1.12 and others	115 days	$7\cdot10^5$
$^{180}_{74}$W	0.14	<20	^{181}W	Electron capture γ 0.132, 0.136	145 days	$7\cdot10^2$
$^{182}_{74}$W	26.2	0.5	^{183m}W	Isomeric transition	5.5 sec	$2.6\cdot10^4$
		20	^{183}W	stable		
$^{183}_{74}$W	14.3	11	^{184}W	stable		
$^{184}_{74}$W	30.7	—	^{185m}W	Isomeric transition γ 0.165, 0.130	1.6 min	—
		2	^{185}W	β^- 0.430	75.8 days	$3\cdot10^3$
$^{186}_{74}$W	28.7	36	^{187}W	β^- 1.33, 0.63, 0.34 γ 0.68 and others	24 h	$2\cdot10^6$

8 h for chemical processing, a 50% chemical yield and finally beta-counting with a conventional counter, a limit of detection of 10^{-10} g for tantalum and 10^{-11} g for tungsten is possible. In practice adequate sensitivity was usually obtained with irradiation periods of 36 h. The chemical separation was designed to isolate the short half-life (24 h) tungsten before 115 day half-life tantalum.

EXPERIMENTAL

Irradiation

Samples and standards were weighed into clean, dry silica ampoules prepared from thin walled silica tubing of 4-mm internal diameter[17]. The ampoules were sealed and samples and standards were packed together into an aluminium can and irradiated in the "self-serve" position in BEPO. Rock samples and stony meteorites were ground to pass a 100-mesh B.S. sieve. Iron meteorites and standard iron and steel samples were irradiated as turnings or single pieces of the metal. The preparation of samples for irradiation is discussed in some detail below.

Standards

Both tantalum and tungsten have appreciable neutron capture cross-sections in the thermal region of the pile neutron spectrum (Ta = 22 barns, W = 18 barns) and in addition, both elements show resonance peaks of more than 10,000 barns in the intermediate or epithermal region of the spectrum[18]. As a result the possibility of self-shielding during irradiation, leading to a reduction of the effective neutron flux through a sample and causing unequal activation of samples and standards, cannot be neglected. To investigate this phenomenon varying weights of the pure oxides of tantalum and tungsten were irradiated simultaneously in BEPO and the induced specific activities were determined (Table II). The results show a decrease in specific activity with increase in sample weight (indicative of self-shielding) and illustrate the unsuitability of pure tantalum and tungsten compounds as standards in the determination.

The effect of self-shielding may be overcome by diluting the absorbing element with material of low cross-section, such as water, silica, alumina or sucrose. Homogeneous solid dilutions are difficult to prepare and a series of aqueous dilutions were made and investigated. Sealed silica ampoules containing dilutions of tantalum as

TABLE II

SELF-SHIELDING EFFECTS IN THE IRRADIATION OF SOLID TANTALUM AND TUNGSTEN OXIDES

Weight Ta_2O_5(mg)	*Specific activity counts per minute per mg Ta*	*Weight WO_3(mg)*	*Specific activity counts per minute per mg W*
2.7	121000	1.9	72400
5.8	113500	4.0	66500
14.9	112500	11.5	63500
19.8	111000	14.3	62300
25.7	109000	19.8	62500
30.6	108500	25.4	60200
38.3	107500	36.7	56500
40.6	105000	40.3	59200
55.1	103000	48.3	57900

the oxalate complex in oxalic acid solution and tungsten as ammonium tungstate in dilute ammonia were irradiated and the specific activity determined (Table III).

TABLE III

SELF-SHIELDING EFFECTS IN THE IRRADIATION OF DILUTE SOLUTIONS CONTAINING TANTALUM AND TUNGSTEN

Weight mg Ta per g solution	*Specific activity counts per minute per mg Ta*	*Weight mg W per g solution*	*Specific activity counts per minute per mg W*
6.09	$5.81 \cdot 10^3$	0.485	$55.5 \cdot 10^3$
6.09	$5.92 \cdot 10^3$	0.485	$54.8 \cdot 10^3$
2.44	$5.97 \cdot 10^3$	0.0245	$53.3 \cdot 10^3$
2.44	$5.88 \cdot 10^3$	0.0245	$52.8 \cdot 10^3$
0.609	$5.95 \cdot 10^3$	0.00245	$57 \cdot 10^3$
0.0609	$5.95 \cdot 10^3$		

No significant change in activity was detectable over the range of dilutions examined, and solutions containing tungsten and tantalum at lower concentrations than the maximum considered in Table III were used in this work. The neutron capture cross-sections of the sample matrix materials, mainly silica or iron, for the pile flux spectrum are sufficiently low for this phenomenon to be neglected with the small sample weights employed.

Fresh liquid standards were prepared on alternate weeks by dilution of gravimetrically standardised carrier solutions with oxalic acid solutions prepared from demineralised water. In practice mixed standards containing both tantalum and tungsten were irradiated and after irradiation subjected to the full chemical separation and purification procedure. Standard solutions for irradiation contained appreciable quantities of oxalic acid, essential to stabilise the tantalum oxalate complex, and it was necessary to investigate the possibility of "blank" contributions brought about by traces of tantalum and tungsten present in this compound. Analysis of the batch of oxalic acid used throughout the work gave a tantalum content of 0.0005 p.p.m. and a tungsten content of 0.05 p.p.m. Contributions from this level of impurity could be neglected.

Dissolution

The methods employed to bring the irradiated samples into solution in the presence of carriers were dependent on the nature of the sample. Rocks and stony meteorites were brought into solution by sintering with sodium peroxide for 10 min at 480 ± 20°[19], in a nickel crucible of 5-ml capacity. Mineral acid mixtures containing hydrofluoric acid were used for iron meteorites and iron and steel samples.

Outline of the radiochemical procedure

A number of radiochemical procedures for tantalum and tungsten have been described[20,21] including one for the separation of tungsten from a tantalum target[21]. The latter method utilises the ethyl acetate extraction of stannous chloride reduced tungsten thiocyanate and isolates tungsten rapidly and in good yield. This method was investigated initially when, after extraction of tungsten, difficulties were experienced in separating tantalum cleanly from the aqueous phase containing several times its weight of tin and boric acid. Tantalum yields were found to be less erratic when zinc dust was substituted for stannous chloride as reducing agent but the procedure was still slow and tedious. The method adopted and used for most of the work was based on the technique of STEVENSON AND HICKS[22] for the di-isopropyl ketone (DIPK) extraction of tantalum from solutions 0.4 *M* in hydrofluoric acid and 6 *M* in sulphuric acid. Using a radiochemical procedure based on this method these authors claim decontamination factors of better than 10^5 for tantalum from fission products. Partition coefficients for tungsten under conditions of maximum tantalum decontamination were determined and found to be 0.1. Subsequently supplies of DIPK failed and methyl isobutyl ketone (hexone) was substituted for it in the extraction[23]. Using identical conditions of acidity, partition coefficients for the tungsten extraction of 0.07 were obtained. Any niobium associated with tantalum in the samples will follow tungsten in the separation whether DIPK or hexone is used as solvent.

Solutions of a number of complexing agents for the back extraction of tantalum from the organic phase after separation were considered. Solutions of oxalic, tartaric, citric and lactic acids, hydrochloric acid–boric acid mixtures, water and hydrogen peroxide solutions of varying concentration were investigated. Five per cent v/v hydrogen peroxide was found to be the most satisfactory reagent, one extraction being sufficient to recover the tantalum where the organic phase was DIPK, hexone requiring two.

Procedures for source mounting tantalum as its oxide prior to β-counting have been described[20,21], but the process requiring a high temperature ignition stage to dehydrate the oxide and subsequent grinding to obtain the oxide in a suitably powdered form for spreading on a counting tray, was inconvenient. A search for an alternative compound was made and the material eventually selected was tri-2,2′-dipyridyl ferrous fluorotantalate, $Fe(dipy)_3(TaF_6)_2$, where (dipy) is 2,2′-dipyridyl[24,25]. The thermal stabilility, solubility in hydrofluoric acid and dependence of the constitution of the compound on the acid strength of the precipitating medium had not been described and were investigated. The compound was found to be thermally stable at temperatures of up to 200°, to have a minimum solubility at room temperatures of 23 mg per 100 g in 0.1 *N* hydrofluoric acid and its composition was independent of acid strength when precipitated in solutions of up to 18 *N* hydrofluoric acid concentration. The compound was not hygroscopic. Despite its relatively high solubility the material was found to fulfil satisfactorily the requirements of a source for beta-counting.

Procedures for mounting tungsten as the compound with 8-hydroxyquinoline[20] and the oxide[21] have been described. The same objections to the use of the oxide apply as in the case of tantalum pentoxide and the oxinate was used in this work. Precipitation was carried out in hot neutral or slightly alkaline solution and was followed immediately by acidification with acetic acid.

The method finally adopted for the isolation and radiochemical purification of the elements may be outlined as follows. Samples and standards are taken into solution in the presence of carriers and tantalum and tungsten co-precipitated by tannin and cinchonine. The precipitate is removed by filtration, washed with 2% ammonium chloride solution and treated with nitric and sulphuric acids to destroy organic matter. Nitric acid is removed by fuming with sulphuric acid and the mixed hydrated oxides precipitated by the addition of water to the cooled sulphuric acid solution. The oxides are dissolved in a solution 0.4 M in hydrofluoric acid and 6 M in sulphuric acid and tantalum removed by solvent extraction with DIPK or hexone.

Tungsten is recovered from the aqueous phase and freed from traces of the solvent by digestion with nitric acid. The precipitated oxide is washed and put through a series of ammonia/nitric acid cycles before being mounted for counting as the oxinate.

Tantalum is backwashed from the organic phase with 5% hydrogen peroxide and hydrated tantalum pentoxide precipitated with ammonia. The extraction cycle is repeated, and finally the hydrated oxide is dissolved in the minimum volume of hydrofluoric acid before precipitation as tri-2,2′-dipyridyl ferrous fluorotantalate for measurement of the induced activity present.

Measurement of radioactivity

The activity present in the sources prepared for counting was measured by either beta- or gamma-counting. A conventional end-window Geiger counter assembly was used for beta-counting. Gamma activities were measured and the spectra of ^{182}Ta and ^{187}W recorded with the aid of a 100 channel, sodium iodide crystal, scintillation spectrometer.

Tantalum emits beta particles of maximum energy 0.53 MeV and 80% of the beta particles emitted by ^{187}W have a maximum energy of 0.63 MeV. It was necessary therefore, to investigate whether corrections to the observed counting rates caused by self-absorption of the beta particles emitted by the source materials were applicable. The effect of self-absorption was determined by preparing sources of varying thickness from common stocks and recording the apparent specific activities (Table IV). In practice sources of between 10 and 15 mg per square centimetre were used, and while the effects for ^{187}W within this range could be neglected, corrections for ^{182}Ta were appreciable.

TABLE IV

SELF-ABSORPTION AND SCATTERING EFFECTS IN TANTALUM AND TUNGSTEN SOURCE MATERIALS

Tungsten oxinate		*Tri-2,2′-dipyridyl ferrous fluorotantalate*	
Source wt. (mg per sq.cm)	*Counts per minute per mg*	*Source wt. (mg per sq.cm)*	*Counts per minute per mg*
1.67	97	1.68	120
2.20	103	2.93	126
3.43	109	4.00	125
5.20	110	6.27	123
7.30	108	7.67	117
8.51	110	8.82	116
10.75	102	9.45	116
14.42	99	13.32	105
18.17	93	17.48	98

Investigation of radiochemical purity

Three checks on the radiochemical purity of the final sources are applicable, namely: the construction of decay curves for the radioactivity emitted by the nuclide; determination of the maximum beta particle energy and comparison of the general shape of the beta absorption curves with those obtained from standards of known radiochemical purity; examination of the gamma ray spectrum. The construction of decay curves and beta absorption curves is facilitated by the availability of automatic counting equipment, and the gamma spectra of relatively weak sources of activity may be readily obtained with multi-channel gamma spectrometers. The application of two of these checks is usually sufficient to indicate the radiochemical purity of the source.

Decay curves for ^{187}W ($t_{\frac{1}{2}} = 24$ h) were always recorded and if sufficient radioactivity was present in the source, as was almost invariably the case, the decay was followed for at least five half-lives (Fig. 1). Gamma spectra, using a 100-channel

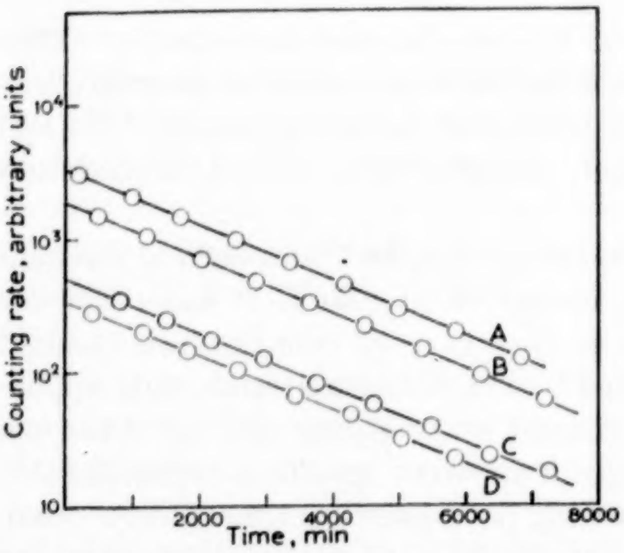

Fig. 1. Decay curves for ^{187}W (half-life 24 h). Curves A and B standards. Curves C and D Skaergaard Intrusion Sample E.G. 4327.

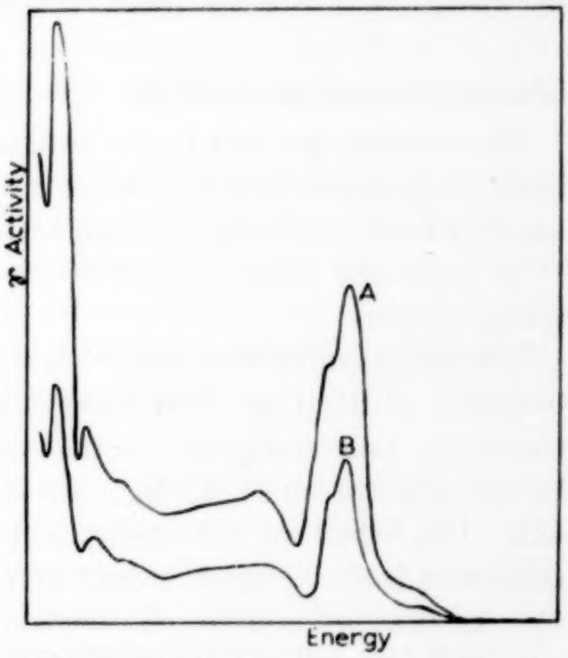

Fig. 2. Gamma spectra for ^{182}Ta. A, standard; B, sample G1.

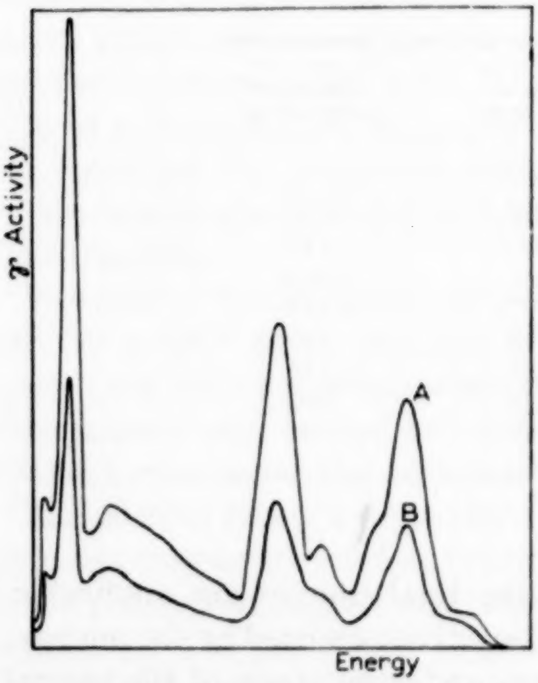

Fig. 3. Gamma spectra for ^{187}W. A, standard; B, sample G1.

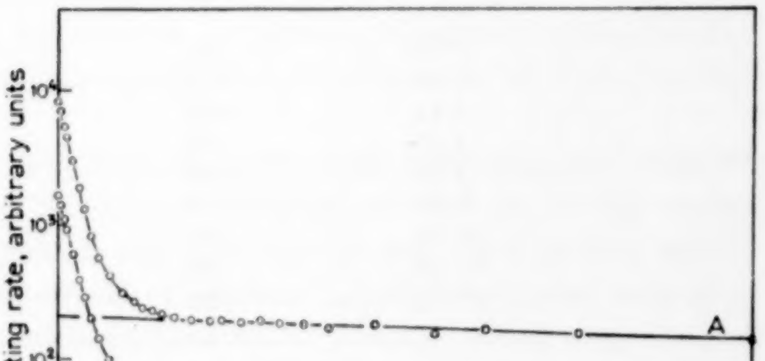

Fig. 4. Absorption curves for ^{182}Ta. Curve A, standard; curve B, ^{182}Ta from sample G1.

spectrometer, were constructed and compared with those obtained from the standards in the determination for both tantalum and tungsten (Figs. 2 and 3). The half-life of ^{182}Ta ($t_{\frac{1}{2}}$ = 115 days) is too long for a decay curve to be prepared as an adjunct to a routine determination and as additional confirmation of the radiochemical purity of this nuclide beta absorption curves may be prepared (Fig. 4).

METHOD

Preliminary treatment of silicate materials

If the sample for analysis consists of silicate material grind it as finely as possible, but certainly to less than 100 B.S. sieve size. Weigh suitable amounts (usually 40–80 mg) into clean, dry silica ampoules and seal the tubes. Mark the ampoules with paint and pack into 3″ aluminium BEPO cans together with standards for irradiation in BEPO. After irradiation allow two hours for the short lived activities to decay before bringing the can back to the laboratory in a shielded container. Carry out the initial operations of the chemical separation behind lead shielding. The number of operations necessarily performed in this way will depend on the nature of the sample and its irradiation period.

Open the sample ampoules and carefully transfer the contents to a nickel crucible of 5-ml capacity containing a layer of sodium peroxide. Thoroughly mix the contents of the ampoules with the sodium peroxide using a nickel spatula, cover with a further layer of sodium peroxide and place for 10 min in a furnace maintained at 480° ± 20°. Remove the crucible and cool rapidly by dipping the outside in water. Invert the crucible and tap the base to detach the sinter cake. Transfer the cake to a 250-ml beaker containing 35 mg of tantalum as the oxalate complex, 35 mg of tungsten as sodium tungstate, 10 ml of 20% tartaric acid and 70 ml of distilled water containing 5 g of ammonium chloride. As soon as the initial violent reaction has abated rinse the nickel crucible, add the washings to the beaker and acidify with 10% v/v sulphuric acid. A clear solution should be obtained at this stage. Boil the weakly acid solution and add ammonia dropwise until it is just alkaline followed by 50% hydrochloric acid until the solution is acid and then two drops in excess. Add 50 ml of hot 2% tannin solution slowly and with constant stirring and boil gently to coagulate the precipitate before removing from the hot-plate. Add 10 ml of 5% cinchonine in 25% hydrochloric acid to the hot solution slowly and with constant stirring and leave to stand for at least thirty minutes before filtering through an 11-cm Whatman No. 541 filter paper. Wash the precipitate with hot 2% ammonium chloride solution and discard the washings.

Preliminary treatment of iron material

Metallic samples and iron meteorites are usually supplied as turnings or small pieces cut from the parent sample. As the tools used in preparing the samples frequently contain high concentrations of tungsten, the possibility of surface contamination of the sample cannot be ignored and must be eliminated by cleaning. Briefly etch the samples with dilute hydrochloric acid containing a little hydrogen peroxide, wash thoroughly with demineralised water and finally with acetone before drying. Weigh 50–100 mg of the samples into clean, dry silica ampoules, seal and pack into 3″ aluminium BEPO cans and irradiate together with standards. When the irradiation has been completed dissolve the metallic samples in the presence of carriers, tartaric and hydrofluoric acids, the acids used for dissolution depending on the sample. During dissolution a little oxidising agent (nitric acid) is added, if not already present, to re-oxidise any reduced tungsten. After the necessary adjustments to the acidity and the addition of 5 g of ammonium chloride, tantalum and tungsten are precipitated is above.

Preliminary treatment of standards

Transfer duplicate small volumes of the standard solution to clean, weighed silica ampoules. Centrifuge to deposit the solution at the lower end of the ampoule, weigh and seal. Irradiate standards and samples together. The standard solutions employed usually contain higher concentrations of tantalum and tungsten than the samples and to avoid the possibility of cross contamination it is advisable to process the samples, at least to the separation stage, before dealing with the standards.

Centrifuge the standard ampoules and open carefully to prevent losses caused by the build up of pressure during irradiation. Remove the solution with a dropping pipette, rinse the last traces of standard from the inside of the ampoule with warm, dilute oxalic acid solution and transfer the mixed standard and washings to a 250-ml beaker containing tantalum and tungsten carrier solutions and tartaric acid.

From this stage the chemistry performed for the separation and isolation of tantalum and tungsten from the standards is identical with that used for the samples.

Separation

Transfer the washed tannin-cinchonine precipitate of tantalum and tungsten to a 250-ml beaker and add 20 ml of concentrated nitric acid and 5 ml of concentrated sulphuric acid. Heat on the hot-plate until all the organic material is destroyed, adding more nitric acid when necessary. Fume to remove excess of nitric acid. Cool and precipitate the hydrated oxides of tantalum and tungsten by the addition of 50 ml of demineralised water. Add 5 ml of concentrated hydrochloric acid, boil, and and spin in a centrifuge to remove the oxides. Treat the precipitate with 10 ml of a solution 0.4 M in hydrofluoric acid, and 6 M in sulphuric acid, rejecting any insoluble residue.

Add the acid solution containing the tantalum and tungsten to a 100-ml separating funnel and shake for 2 min with 10 ml of DIPK (or hexone) previously conditioned with 0.4 N hydrofluoric acid 12 N sulphuric acid. Remove the aqueous phase and extract with a further 10 ml of the conditioned organic solvent. Combine the organic phases and shake briefly with 10 ml of the mixed acid solution. Retain the aqueous phase and combine it with the parent solution. The tungsten present is contained in the combined aqueous phases and tantalum in the organic solvent.

Procedure for tungsten

Combine the aqueous phases from the separation in a 150-ml beaker, add 15 ml of concentrated nitric acid and digest on a hot-plate in a good fume cupboard. Isolate the precipitated tungsten oxide by spinning in a centrifuge, wash the precipitate with hot concentrated nitric acid and reject the washings. Dissolve the oxide in 0.880 M ammonia solution, dilute to 15 ml, spin in a centrifuge and discard the residue, if any. Digest on a water bath with concentrated nitric acid to precipitate tungsten oxide, wash the precipitate, dissolve in the minimum volume of 0.880 *M* ammonia solution, spin in a centrifuge and reject any residue. The tungsten oxide–ammonium tungstate cycle may be repeated and combined with ferric hydroxide scavenges should this be necessary to achieve radiochemical purity.

Precipitate tungsten oxinate in boiling, slightly alkaline solution by the slow addition of 1 ml of 5% 8-hydroxyquinoline solution in 2 *N* acetic acid. After the addition of 8-hydroxyquinoline acidify the solution with acetic acid, remove tungsten oxinate by spinning in a centrifuge, wash with water and finally alcohol and slurry onto a weighed counting tray with a little alcohol. Dry under an infra-red heating lamp, weigh for chemical yield determination and count. Chemical yields are normally within the range 40–60%.

Procedure for tantalum

Shake the combined DIPK extracts from the separation with 10 ml of 0.4 *N* hydrofluoric acid/12 *N* sulphuric acid solution in a 100-ml separating funnel and reject the aqueous phase. Add 10 ml of 5% hydrogen peroxide solution and shake for 2 min. Transfer the aqueous phase to a 100-ml beaker, add 1 drop of phenolphthalein solution followed by 0.880 ammonia until the solution is just pink, dilute to 50 ml and heat on a hot-plate until hydrogen peroxide is destroyed and precipitation of hydrated tantalum pentoxide is complete. Isolate the oxide by spinning in a centrifuge, dissolve in 10 ml of 0.4 *N* HF/12 *N* H_2SO_4 solution and re-extract with conditioned DIPK rejecting the aqueous phase. Back extract into 5% hydrogen peroxide solution and precipitate with ammonia as before. Dissolve the hydrated oxide in the minimum volume of 40% hydrofluoric acid (1–2 drops), dilute to 5 ml with demineralised water and add 10 drops of 0.1 molar tri-2,2′-dipyridyl ferrous sulphate. Spin in a centrifuge to isolate the precipitate, wash with 5 ml of demineralised water and finally with alcohol. Slurry with a little alcohol onto a tared counting tray, remove the solvent by heating under a lamp, weigh for chemical yield determination and count. Chemical yields of 40–60% are normal.

Where hexone is used instead of DIPK in the separation, back extraction with hydrogen peroxide sometimes results in emulsification. The emulsion is readily broken by spinning in a centrifuge.

Calculations

Count the samples and standards and correct the measured activities for background, counter dead-time, and with tungsten, for decay during counting. The amount of tantalum or tungsten present in the sample *X*, is given by the relation:

$$\frac{\text{Mass of } X \text{ in sample}}{\text{Mass of } X \text{ in standard}} = \frac{\text{Activity from } X \text{ in sample corrected for } 100\% \text{ chemical yield}}{\text{Activity from } X \text{ in standard corrected for } 100\% \text{ chemical yield}}$$

Confirm the radiochemical purity of the final source by means of half-life determinations (for tungsten), beta absorption curves and gamma spectra.

ACCURACY AND PRECISION

Some idea of the precision of the method developed when applied to the determination of tantalum and tungsten at sub-microgram levels may be obtained from

TABLE V

THE TANTALUM AND TUNGSTEN CONTENT OF G1 AND W1

Sample	*Tantalum (p.p.m.)*	*Average (p.p.m.)*	*Tungsten (p.p.m.)*	*Average (p.p.m.)*
G1	1.63, 1.54, 1.54, 1.56, 1.57, 1.54, 1.61, 1.74	1.59	0.40, 0.47, 0.41, 0.37, 0.37, 0.36, 0.41	0.40
W1	0.47, 0.48	0.48	0.42, 0.42, 0.41, 0.47	0.43
G1 (Ground by authors)	1.29, 1.37	1.33	0.11, 0.12	0.12

TABLE VI

TANTALUM AND TUNGSTEN CONTENTS OF SAMPLES FROM THE SKAERGAARD INTRUSION OF EAST GREENLAND AND OF TWO DUNITES

Sample and origin	*Ta content (p.p.m.)*	*Average (p.p.m.)*	*W content (p.p.m.)*	*Average (p.p.m.)*
E.G. 3058 transgressive granophyre sill	1.29, 1.33, 1.34	1.32	0.41, 0.45, 0.45, 0.48, 0.50	0.46
E.G. 4332 hedenbergite granophyre	3.33, 3.60, 3.66	3.53	1.02, 1.02, 1.07, 1.14, 1.16, 1.16, 1.17	1.11
E.G. 4329 purple band ferrogabbro	1.35, 1.63	1.49	0.41, 0.43, 0.47	0.44
E.G. 4328 purple band ferrogabbro	1.26, 1.30, 1.36	1.31	0.18, 0.19, 0.20, 0.21	0.20
E.G. 4327 purple band ferrogabbro	0.90, 0.99	0.95	0.31, 0.52	0.42
E.G. 4318 lower ferrogabbro	0.55, 0.62	0.59	0.37, 0.46	0.42
E.G. 5196 hortonolite ferrogabbro	1.52, 1.53, 1.60	1.55	0.08, 0.08, 0.10, 0.10	0.09
E.G. 5181 hortonolite ferrogabbro	0.40, 0.45	0.43	0.12, 0.12	0.12
E.G. 4427 middle gabbro	1.09, 1.14	1.12	0.12, 0.12	0.12
E.G. 5086 hypersthene-olivine gabbro	0.33, 0.43	0.38	0.13, 0.14	0.14
E.G. 4507 chilled marginal gabbro	0.43, 0.45, 0.45, 0.45, 0.45, 0.45, 0.46, 0.53	0.46	0.17, 0.19, 0.20, 0.20, 0.20, 0.22, 0.23, 0.23, 0.23, 0.24, 0.24, 0.25	0.22
Dunite A. 301	0.022, 0.027	0.025	0.14, 0.15	0.15
Dunite S. 39	0.010, 0.012	0.011	0.42, 0.48	0.45

TABLE VII

TANTALUM IN STANDARD STEEL SAMPLES

Sample	*Published tantalum content (%)**	*Tantalum content by activation (%)*	*Average tantalum content by activation (%)*
B.C.S. 246 '18/12' Stainless Steel	< 0.02	0.0283, 0.0285	0.028
B.C.S. 271 Mild Steel	0.008	0.0032, 0.0032	0.003
B.C.S. 272 Mild Steel	0.0015	0.0007, 0.0008	0.0008
B.C.S. 273 Mild Steel	0.020	0.0129, 0.0133	0.013
B.C.S. 274 Mild Steel	0.0065	0.0038, 0.0041	0.004
B.C.S. 275 Mild Steel	0.003	0.0025, 0.0031	0.003
N.B.S. 123B Stainless Steel Nb–Ta stabilised	0.20	0.179, 0.189, 0.194 0.205, 0.209, 0.216	0.20

* not claimed by manufacturers to be more than approximate except in case of NBS 123B.

TABLE VIII

TUNGSTEN IN STANDARD STEEL SAMPLES

Sample	*Published tungsten content (average) (%)*	*Tungsten content by activation (%)*	*Average tungsten content by activation (%)*
B.C.S. 246 '18/12' Stainless Steel	0.22	0.181, 0.188, 0.182, 0.174, 0.185	0.18
B.C.S. 271 Mild Steel	0.015	0.011, 0.011, 0.014, 0.014	0.013
B.C.S. 272 Mild Steel	< 0.01	0.0013, 0.0013	0.0013
B.C.S. 273 Mild Steel	0.28	0.278, 0.300	0.29
B.C.S. 274 Mild Steel	0.04	0.0299, 0.0321, 0.0358, 0.0363	0.034
B.C.S. 275 Mild Steel	0.05	0.0392, 0.0410, 0.0436, 0.0442	0.042
B.C.S. 276 Mild Steel	0.205	0.208, 0.212	0.21
B.C.S. 277 Mild Steel	0.125	0.122, 0.131	0.13
N.B.S. 123B Stainless steel Nb–Ta stabilised	0.18	0.160, 0.161, 0.161, 0.167	0.16

the results for the analyses of the granite G1 and the diabase W1 recorded in Table V and the results for samples from the Skaergaard Intrusion (Table VI). Attempts to assess the accuracy of the method are hampered by the lack of suitable standard materials whose trace element content has been unequivocally established. A number of commercially available standard steel samples containing low concentrations of tantalum and tungsten are available and were examined (Tables VII and VIII).

It must be emphasised that the published results for the tantalum contents of the British Chemical Standard steels examined are not claimed by the manufacturers to be anything more than approximate. Only one steel sample (N.B.S. 123B) with a low, accurately known tantalum content was available and with this sample excellent agreement between the observed and published tantalum contents was obtained. The agreement between the published and observed tungsten contents of the steel samples examined was satisfactory.

RESULTS AND DISCUSSION

FAIRBAIRN *et al.*[26] have proposed a granite G1 from Westerly, Rhode Island, and a diabase W1 from Centerville, Virginia as international standards for the determination of major and minor constituents of igneous rocks. Uniform samples of G1 and W1 supplied pulverised by the U.S. Geological Survey were available and on analysis gave the results listed in Table V. In addition a lump of the parent rock was available in the case of G1. Pieces totalling approximately 10 g in weight were removed from the parent rock sample, broken down in a mild steel percussion mortar and hand picked to exclude any pieces forming a part of the original surfaces. Finally the sample was further broken down in the percussion mortar before being ground in agate, sampled and analysed. The results for this material are also included in Table V.

In view of the small sample weight taken initially and the subsequent hand picking, these results are open to objection on the grounds of the possible inhomogeneity of the parent sample. However, the tantalum and especially tungsten contents obtained in a sample of G1 ground in the authors' laboratory are significantly lower than those from samples ground by the U.S. Geological Survey.

The possibility that the sample may have become contaminated after receipt in the authors' laboratory was considered unlikely in view of the precautions exercised. As soon as the sample was received it was subdivided into a series of clean, dry, numbered sample tubes. No significant differences in the tantalum and tungsten contents of G1 were detectable whichever sample tube was used as a source of the sample. During the course of the work described in this paper a further batch of G1 was received into the laboratory. Results obtained on the new batch of material were no different from those obtained with the previous batch.

A series of rock samples from the Skaergaard Intrusion of East Greenland (kindly supplied by Prof. L. R. WAGER, Department of Geology and Mineralogy, University of Oxford) were examined and the results for repeated analyses are included in Table VI. These samples had been ground in the Mineral Dressing Group of the Chemical Engineering Division, Atomic Energy Research Establishment, Harwell, by pulverising in a stainless steel percussion mortar followed by sieving through a 100-mesh sieve. A single small piece of E.G. 4507 (chilled marginal gabbro) was available as well as the finely ground material. This was ground and sampled in the authors' laboratories using the apparatus and method described in the preparation of G1. Analyses of duplicate samples gave tantalum contents of 0.34 and 0.34 p.p.m. and tungsten contents of 0.16 and 0.20 p.p.m. Duplicate samples of the material ground by the Mineral Dressing Section examined at the same time gave tantalum contents of 0.43 and 0.53 p.p.m. and tungsten contents of 0.22 and 0.25 p.p.m. Because of the small samples used these results are open to objection for the same reason as given in the case of G1.

Also included in Table VI are results for the tantalum and tungsten contents of two ultrabasic rocks (dunites). Sample S. 39 from Balsam Quarry, North Carolina, was kindly supplied by Dr. E. A. VINCENT of the Department of Geology and Mineralogy, University of Oxford.

A number of stony and iron meteorites were examined and their results are recorded in Tables IX and X. All of these samples had been prepared for analysis in the authors' laboratory. Johnstown, Ness County, Long Island and Forest City stony

TABLE IX

TANTALUM AND TUNGSTEN CONTENTS OF SOME STONY METEORITES

Sample and origin	*Tantalum (p.p.m.)*	*Average (p.p.m.)*	*Tungsten (p.p.m.)*	*Average (p.p.m.)*
Johnstown, Weld Co., Colorado	0.007, 0.009	0.008		
Ness Co., Kansas	0.022, 0.022	0.022		
Long Island – Phillips Co., Kansas	0.027, 0.027	0.027		
Forest City, Winnebago Co., Iowa	0.022, 0.023	0.023		
Chateau Renard	0.024, 0.025, 0.027, 0.030	0.027	0.15, 0.15, 0.17	0.16
Holbrook, Arizona	0.024, 0.026	0.025	0.15, 0.15	0.15
Chandakaphur	0.018, 0.019, 0.020, 0.022	0.020	0.11, 0.12, 0.13	0.12
Bjurböle	0.020, 0.021	0.021	0.07, 0.09	0.08
Tabory (Ochansk)	0.018, 0.018	0.018	0.14, 0.19	0.17

TABLE X

TANTALUM AND TUNGSTEN CONTENTS OF SOME IRON METEORITES

Sample and origin	*Tantalum (p.p.m.)*	*Average (p.p.m.)*	*Tungsten (p.p.m.)*	*Average (p.p.m.)*
Canyon Diablo	0.0009, 0.001, 0.003, 0.004	0.002	1.42, 1.54, 1.87	1.61
Henbury	0.004, 0.005	0.005	0.75, 0.77	0.76
San Martin	0.0006, 0.0009	0.0008	2.60, 2.68	2.64

meteorite samples were available from earlier work. These samples had been drilled with a tungsten carbide tipped drill and in view of the possibility of tungsten contamination during this operation no results for this element have been recorded. The other stony meteorites examined had been broken down in a mild steel percussion mortar and ground in a new agate mortar. Iron meteorites were cut into small pieces with a hacksaw, washed with dilute hydrochloric acid and acetone and stored in an airtight bottle. Before sampling for irradiation, iron meteorite samples were given a further surface etch with a dilute hydrochloric acid–hydrogen peroxide solution and then washed with de-ionised water and finally acetone.

In view of the precautions exercised in the preparation of meteorite samples, it is considered that significant contamination is unlikely. Results obtained by the analysis of G1 and E.G. 4507 ground in the authors' laboratory were in all cases lower than results obtained on samples of these materials which were received into the laboratory already ground. Consequently the tantalum and tungsten contents for G1 supplied by the U.S. Geological Survey and all the Skaergaard Intrusion samples in Table VI must be regarded as accurate in a relative sense only. While these results represent the tantalum and tungsten contents of the samples as received, it is possible that they may not represent the absolute contents of the natural rock samples.

Clearly the use of G1 as a standard for intercomparison purposes is still valid, and as pointed out earlier the low values, obtained on small pieces only may well be local values and not truly representative. Nevertheless from the evidence, it seems clear that the greatest care is necessary in the preparation for analysis of geological specimens required for trace tungsten and tantalum determinations.

POSSIBLE INTERFERING ELEMENTS

Methods for the production of ^{182}Ta and ^{187}W other than by the (n, γ) reaction may be postulated. These alternative methods of formation represent potential sources of error in the determination. Amongst the reactions likely to introduce errors into the determination may be mentioned the (n, p) and (n, α) reactions brought

TABLE XI

CONFLICTING NUCLEAR PROCESSES IN THE ESTIMATION OF TANTALUM AND TUNGSTEN BY (n, γ) REACTION

Parent isotope	*Abundance (%)*	*Reaction*	*Product*
$^{182}_{74}$W	26.5	(n, p)	$^{182}_{73}$Ta
$^{185}_{75}$Re	37.1	(n, α)	$^{182}_{73}$Ta
$^{183}_{74}$W	14.3	(γ, p)	$^{182}_{73}$Ta
$^{187}_{75}$Re	62.9	(n, p)	$^{187}_{74}$W
$^{190}_{76}$Os	26.4	(n, α)	$^{187}_{74}$W

about by the more energetic component of the neutron flux and the (γ, p) reaction induced by the pile gamma flux.

Some of the more important reactions (other than the (n, γ)) which can lead to the production of ^{182}Ta and ^{187}W are listed in Table XI. The elemental abundances of tungsten, rhenium and osmium are low and unless the reactions enumerated have exceptionally high cross-sections, interference at any significant level is unlikely to be serious. An upper limit to the radioactivity produced by the conflicting nuclear reactions listed in Table XI may be determined by irradiating pure samples of tungsten, rhenium and osmium or their compounds and determining the ^{182}Ta and ^{187}W activities present in them (Table XII). Any tantalum or tungsten present as impurities in the samples examined in Table XII will contribute by (n, γ) reaction to the activity produced, and in consequence the results included in the table are to be regarded as a maximum.

TABLE XII

APPARENT TANTALUM CONTENT OF TUNGSTEN AND RHENIUM AND THE APPARENT TUNGSTEN CONTENT OF RHENIUM AND OSMIUM

Element	*Apparent tantalum content (average) (p.p.m.)*	*Apparent tungsten content (average) (p.p.m.)*
Tungsten	0.23	—
Rhenium	4.4	3.54
Osmium	—	1.32

The value of the upper limit of interference caused by conflicting nuclear processes on tungsten, rhenium and osmium determined above, coupled with a knowledge of the approximate contents of these elements likely to be encountered in any of the samples analysed, suggests that errors produced by them are insignificant and can be ignored.

CONCLUSION

The method whose development and application has been described in this paper has been applied to the determination of tantalum at levels down to $8 \cdot 10^{-10}$ g and tungsten down to $2 \cdot 10^{-9}$ g. These results represent the maximum sensitivity obtainable for tantalum with the short irradiation periods used: the tungsten sensitivity could have been extended if necessary. Longer irradiations with the existing facility would enable the sensitivity to be improved and there is every indication that the sensitivities quoted in the section on nuclear data could be attained. No radiochemical impurity has been detected in any of the final sources from the variety of samples examined.

SUMMARY

A method for the determination of sub-microgram amounts of tantalum and tungsten in rocks and meteorites by neutron activation analysis is described. Radiochemical separation from the components of the irradiated sample was employed to provide sources for measuring ^{182}Ta and ^{187}W by beta and gamma counting and by gamma spectrometry. Determinations of tantalum at the lower limit of $8 \cdot 10^{-10}$ g and tungsten at $2 \cdot 10^{-9}$ g have been made. Amongst the materials examined using the method were the intercomparison rocks G1 and W1, rock samples from the

Skaergaard Intrusion of East Greenland and a number of iron and stony meteorites. In addition a number of standard steel samples of known tungsten content and one of known tantalum content were examined and good agreement was observed between the published results and those determined by activation analysis.

RÉSUMÉ

Une méthode est proposée pour l'ultramicrodosage du tantale et du tungstène dans les rocher et les météorites par activation au moyen de neutrons. Une séparation radiochimique d'avec les composants de l'échantillon irradié a été effectuée en vue de la mesure du ^{182}Ta et du ^{187}W par comptage beta et gamma et par spectrométrie gamma.

ZUSAMMENFASSUNG

Ultramikromengen von Tantal und Wolfram in Gesteinen und Meteoriten können durch Aktivierung mit Neutronen bestimmt werden. Zur Messung von ^{182}Ta und ^{187}W durch Beta und Gamma-Zählung und Gamma-Spektrometrie wurden die Komponenten der bestrahlten Probe nach radiochemischen Methoden abgetrennt.

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SPECTROPHOTOMETRIC DETERMINATION OF URANIUM WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

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INTRODUCTION

Numerous colorimetric reagents have been proposed for uranium determinations. Dibenzoylmethane[1], 2-acetoacetylmethane[2], neothorin[3] (arseneazo) offer high sensitivity, but can be applied only to solutions from which interfering ions have been removed. CHENG AND BRAY[5] recently reported a new, sensitive reagent for uranium, 1-(2-pyridylazo)-2-naphthol (PAN), which reacts with many heavy metals[4-9]. CHENG[7] states that in an alkaline solution containing strong complexing agents, only uranium precipitates when PAN is added. The precipitated uranium was extracted into dichlorobenzene, and the uranium determined spectrophotometrically at 570 mμ. However, he stated that this precipitate is not soluble in chloroform or carbon tetrachloride, hence uranium–PAN complex could not be extracted with chloroform or carbon tetrachloride. The results described below show that the uranyl complex in ammoniacal medium is not completely soluble in chloroform; but in the presence of sodium chloride or sodium sulfate, it can be easily extracted by chloroform.

Apparatus and reagents

All measurements were made with a Model EPV-2 Hitachi spectrophotometer, with 1-cm cells. A Beckman H-2 type pH meter was used.

Standard solution of uranium: This was prepared by dissolving 1.200 g of uranyl nitrate hexahydrate in 1 l of distilled water. It was standardized by the oxine method.

Ethylenediaminetetraacetic acid (disodium salt) (EDTA) solution: A 0.1 *M* aqueous solution was prepared from the reagent grade EDTA.

1-(2-pyridylazo)-2-naphthol solution (PAN): A 0.1% solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in absolute methanol, filtering through glass wool, and diluting to 100 ml with methanol. This solution is stable for several weeks if stored in an amber bottle.

Buffer solution (pH 9.5–10.0): Ammonium chloride–ammonia mixed solution was used for the pH adjustment.

All other chemicals used in this work were pure Wako's reagents.

Procedure

An aliquot of the slightly acid or neutral solution containing 2 to 100 μg of uranium was mixed with 5 ml of the buffer solution, 2 ml of 0.1 *M* EDTA solution and 2.0 g of sodium chloride, and diluted to approximately 20 ml; the pH was adjusted to 9.5–10 with ammonium hydroxide, if necessary. 2 ml of 0.1% PAN was added and allowed to stand for five min. Exactly 10 ml of chloroform was added to the mixture which was then shaken vigorously for 1 to 2 min. The chloroform extract was centrifuged and the absorbance measured at 560 mμ against a reagent blank.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the PAN reagent in chloroform and of the chelate formed with uranium are presented in Fig. 1. These curves were obtained with the addition of 2 ml of 0.1 M EDTA to complex interfering metals, such as copper and zinc. The maximum absorption of the red uranium dye chelates appears at approximately 560 mμ, where the dye itself does not absorb appreciably.

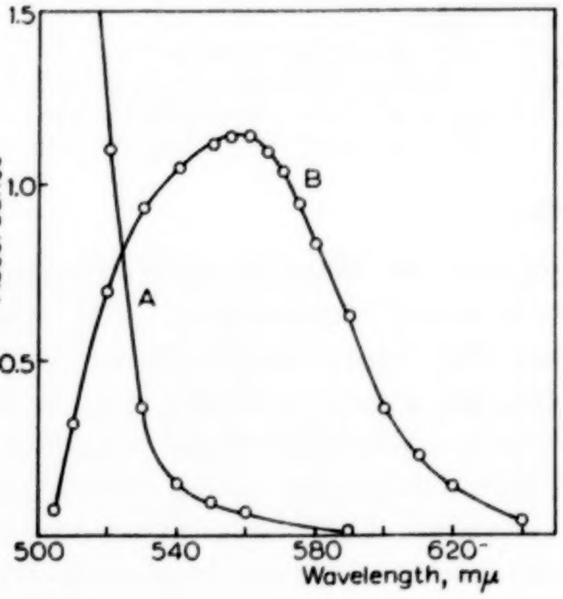

Fig. 1. Absorption spectra of uranium–PAN complex in chloroform. A, uranium(VI)–PAN complex, 12.8 μg U/ml. B, PAN.

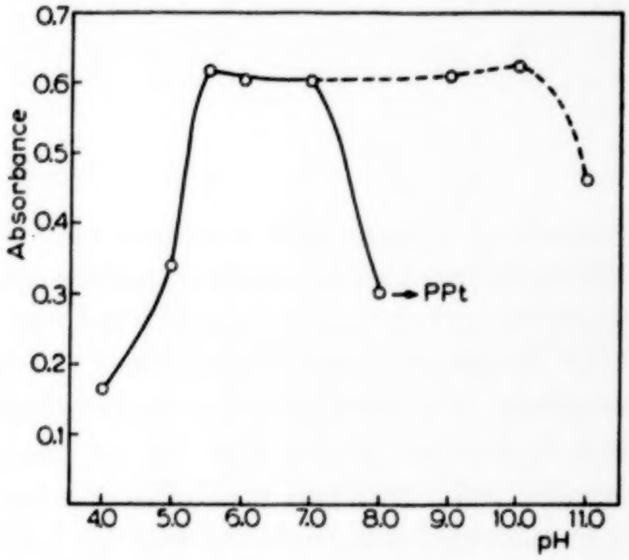

Fig. 2. Effect of pH on absorbance of chloroform extract ——— no sodium chloride, - - - - sodium chloride added ($\lambda = 560$ mμ).

Beer's law

The absorbances of uranium–PAN solution were found to be linearly related to the concentration of uranium. Typical data for a calibration curve are given in Table I.

TABLE I

CALIBRATION DATA FOR COLORIMETRIC URANIUM ANALYSES

Uranium concn., p.p.m.	*Absorbance at 560 mμ*
1.15	0.102
2.30	0.202
4.60	0.408
5.75	0.511
6.90	0.615
8.05	0.718
9.20	0.820

Effect of pH

A series of solutions containing definite amounts of uranyl solution and 1 ml of 0.1% PAN was prepared. Ammonium chloride–ammonium hydroxide or acetic acid–sodium acetate was used for the pH adjustment. Fig. 2 shows that the optimum pH range was from pH 5.5 to 10.0. Below pH 4.0 no significant complex between uranium and PAN was formed. At higher pH (above *ca.* 8.0), the complex formed between uranium and dye could not be extracted completely by chloroform (unless sodium chloride was added) or by carbon tetrachloride.

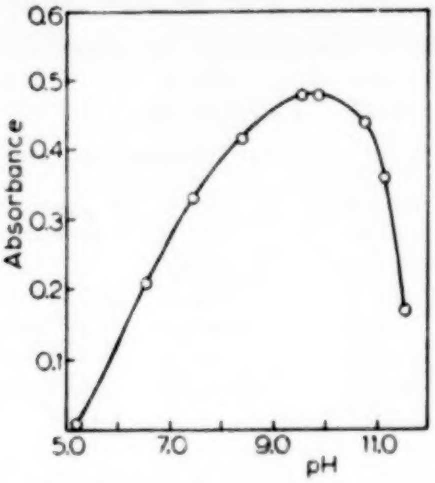

Fig. 3. Effect of pH on absorbance of chloroform extract in the presence of EDTA. Sodium chloride added. (λ = 560 mμ)

A second series of solutions containing definite amounts of uranyl nitrate solution, 2 ml of 0.1 *M* EDTA solution, 2 g of sodium chloride and 2 ml of 0.1% dye solution was prepared. The results are given in Fig. 3. Uranium–PAN complex could be extracted very smoothly by chloroform in the presence of sodium chloride but the optimum pH range was rather narrow (pH 9.5–10). Below pH 6 or above pH 12, no significant complex between uranium and PAN was formed. Because the pH is such a critical factor in obtaining the maximum color development and reproducible results, the pH of the solution should be carefully adjusted to ±0.2 unit, in addition to using a buffer solution.

Effect of complexing agents

Several ml of 0.1% cyanide solution and about 0.1 g of sodium fluoride did not show any effect, but EDTA affected the color development to some degree. EDTA and PAN competed for the uranium when large amounts of free EDTA were present. If only a slight excess of EDTA was present, such competition was overcome by adding more dye. Though uranyl ion forms a stronger complex with PAN than with EDTA, more dye should be added when more EDTA is present. Two or three ml of 0.1% dye solution was satisfactory when 0.5 mmoles of EDTA was present. The amounts of complexing agent added for masking purposes should be slightly in excess. Cyanide is very effective in eliminating interference from copper, nickel and mercury.

TABLE II

EFFECT OF VARIOUS ADDITIONAL SALTS

Salts	*g*	*Absorbance at 560 mμ*
NaCl	2.5	0.572
Na_2SO_4	2.5	0.574
KNO_3	2.5	0.490
KCN	1.0	0.272

Effect of various additional salts on absorbance

Table II shows the effect of various additional salts, and Table III shows the effect of varying the amount of sodium chloride. Sodium chloride or sodium sulfate is the most suitable additional salt; that 1 g of sodium chloride is sufficient to complete the extraction of the uranium–PAN chelate by chloroform.

TABLE III

EFFECT OF AMOUNTS OF SODIUM CHLORIDE

NaCl added *g*	*Absorbance* *at 560 mμ*
1.0	0.574
1.5	0.576
2.0	0.584
2.5	0.572
3.0	0.574

Time of standing

Table IV shows that the minimum time for standing before extraction with chloroform for complete color development of the uranium–PAN complex was five min. After this time the color was very stable and suitable for quantitative work.

TABLE IV

TIME OF STANDING

Time *min*	*Absorbance* *at 560 mμ*
1	0.495
3	0.493
5	0.490
10	0.490

Reproducibility and accuracy

The reproducibility of the method was tested by determining the recovery of 2.0, 5.5, and 9.0 p.p.m. of uranium on 11 successive samples. The results are given in Table V. The standard deviation was calculated using the formula:

$$\text{S. D.}\,\alpha = \sqrt{\frac{(\overline{X} - X)^2}{N - 1}}$$

where $(\overline{X} - X)$ is the deviation of each determination from the average, and N is the total number of determinations.

Interfering ions

To study the effect of various metals on this determination of uranium, a solution containing both uranium and the metal was treated according to the procedure. The results obtained are given in Table VI and VII. The data show that uranium could be determined in the presence of many heavy metals which frequently interfere with other colorimetric methods for uranium.

Chloride, bromide, iodide, sulfate, nitrate, carbonate, acetate and fluoride did not interfere. Phosphate interfered with the color reaction because uranyl phosphate was precipitated.

TABLE V

REPRODUCIBILITY OF THREE CONCENTRATIONS

No.	2.0 p.p.m. U		5.5 p.p.m. U		9.0 p.p.m. U	
	Absorbance vs. blank	*Dev. from mean absorbance*	*Absorbance vs. blank*	*Dev. from mean absorbance*	*Absorbance vs. blank*	*Dev. from mean absorbance*
1	0.179	0.001	0.485	0.003	0.790	0.014
2	0.177	0.003	0.480	0.008	0.800	0.004
3	0.180	0.000	0.490	0.002	0.810	0.006
4	0.177	0.003	0.490	0.002	0.795	0.009
5	0.180	0.000	0.489	0.001	0.815	0.011
6	0.178	0.002	0.491	0.003	0.800	0.004
7	0.181	0.001	0.492	0.004	0.810	0.006
8	0.179	0.001	0.487	0.001	0.805	0.001
9	0.183	0.003	0.490	0.002	0.800	0.004
10	0.179	0.001	0.491	0.003	0.810	0.006
11	0.183	0.003	0.482	0.006	0.805	0.001
Range	0.006		0.009		0.025	
Median	0.180		0.487		0.802	
Mean X	0.180		0.488		0.804	
Av. Dev.	0.0016		0.0032		0.0060	
S. D. α	0.0021		0.0040		0.0075	
% Dev.	1.17		0.82		0.93	

% Dev. $= 100\alpha/\bar{X}$

Further work on the applicability of PAN to the determination of small amounts of uranium in ores and alloys is now in progress.

TABLE VI

DETERMINATION OF URANIUM IN THE PRESENCE OF THORIUM

(59.0 μg uranium taken)

Th added mg	*Uranium μg*	
	Found	*Error*
0.22	59.3	+0.3
0.44	59.7	+0.7
0.66	60.0	+1.0
1.10	61.2	+2.2
2.20	61.3	+2.3

TABLE VII

EFFECT OF METALS ON DETERMINATION OF URANIUM WITH PAN

(59.0 μg uranium taken)

Metal added	*Amt. added mg*	*Added as*	*Complexing agents*	*Uranium μg*	
				Found	*Error*
Ag	1.0	$AgNO_3$	KCN	57.5	− 1.5
As	1.0	K_3AsO_3	EDTA	59.0	± 0.0
Al	1.0	$AlCl_3$	EDTA	59.1	+ 0.1
Al	5.0	$AlCl_3$	EDTA	65.7	+ 6.7
Bi	0.5	$Bi(NO_3)_3 \cdot 5H_2O$	EDTA	61.8	+ 2.8
Ce	1.2	$Ce(NO_3)_3 \cdot 6H_2O$	EDTA	59.0	± 0.0
Cd	1.0	$Cd(NO_3)_2 \cdot 4H_2O$	EDTA	59.7	+ 0.7
Ca	6.0	$CaCl_2$	EDTA	59.5	+ 0.5
Cu	1.0	$CuSO_4 \cdot 5H_2O$	EDTA	57.7	− 1.3
Fe	1.1	$FeCl_3$	EDTA	59.3	+ 0.3
Ga	0.6	$GaCl_3$	EDTA	59.0	± 0.0

Continued

TABLE VII (continued)

Metal added	*Amt. added mg*	*Added as*	*Complexing agents*	*Uranium µg*	
				Found	*Error*
Hg	1.0	$HgCl_2$	KCN	59.0	± 0.0
Mn	1.0	$MnSO_4 \cdot 4H_2O$	EDTA	57.1	− 1.9
Mo	1.1	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	EDTA	58.0	− 1.0
Ni	1.0	$NiSO_4 \cdot 7H_2O$	KCN	59.2	+ 0.2
Zr	0.5	$Zr(SO_4)_2 \cdot 4H_2O$	EDTA + KCN	57.0	− 2.0
Zn	1.0	$ZnSO_4 \cdot 7H_2O$	EDTA	59.2	+ 0.2
Pb	1.0	$Pb(NO_3)_2$	EDTA	59.0	± 0.0
Mg	5.0	$MgCl_2$	EDTA	60.2	+ 1.2
La	0.6	$La(NO_3)_3 \cdot 6H_2O$	EDTA	62.0	+ 3.0
In	0.5	$InCl_3$	EDTA	60.5	+ 1.5
Sn	1.0	$SnCl_4$	EDTA	70.1	+11.1
Ti	0.5	$Ti(SO_4)_2$	EDTA + NaF	63.3	+ 4.3
V	1.3	$Na_3VO_4 \cdot 10H_2O$	EDTA	59.0	± 0.0
W	1.0	$Na_2WO_4 \cdot 2H_2O$	EDTA	57.5	− 1.5

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SUMMARY

1-(2-Pyridylazo)-2-naphthol (PAN) reacts with uranium to form a deep red precipitate in ammoniacal solutions; this can be extracted with chloroform if sodium chloride or sulfate is added and it has a maximum absorption at 560 mµ. The color is stable and follows Beer's law. Trace amounts of uranium may be determined in the presence of many metals without prior separation if strong complexing agents, such as EDTA or cyanide, are added.

RÉSUMÉ

De nombreux cations réagissent avec l'(α-pyridylazo)-1-hydroxy-2-naphtalène; cependant, en présence d'agents complexants, tels que l'acide éthylènediaminotétracétique et le cyanure, seul l'uranium donne un précipité rouge foncé pouvant être extrait par le chloroforme, en présence de chlorure ou de sulfate de sodium.

ZUSAMMENFASSUNG

Uran bildet mit 1-(2-Pyridylazo)-2-naphthol (PAN) in Gegenwart von Komplexbildnern (EDTA, Cyaniden) einen rot gefärbten Niederschlag, der in Gegenwart von Natriumchlorid oder Natriumsulfat mit Chloroform extrahiert werden kann.

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A HETEROMETRIC STUDY OF THE PHENANTHROLINE COMPOUNDS WITH PLATINUM, PALLADIUM AND GOLD HALIDES AND THEIR ANALYTICAL APPLICATION

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INTRODUCTION

1,10-Phenanthroline is known analytically because it forms a complex with iron(II), which is very stable and is used for the spectrophotometric determination of iron. Phenanthroline is also used in the gravimetric determination of palladium and in its separation from platinum[1]. Palladium is precipitated as $PdC_{12}H_8N_2Cl_2$ from hydrochloric acid solution, dried at 110° and weighed. According to RYAN[1], the compound is pale-yellow in colour, very stable, and insoluble in water and most other solvents. Under similar conditions, RYAN found that the gold compound was incompletely precipitated. An attempt to separate palladium from gold by the same procedure was also unsuccessful. DUVAL[1], who studied the chloride compounds of phenanthroline thermogravimetrically, found a temperature limit of 50–389° and added "that the formula of the precipitate changes according to the anion associated with the palladium *before* precipitation". Up till now very little seems to be known about the behaviour and composition of the gold or platinum compounds of phenanthroline.

This investigation was carried out with a double purpose: firstly, to study the reactions between phenanthroline and noble metal halides heterometrically, and secondly, to see if the heterometric method can be used for the determination of platinum, palladium or gold, singly or in mixtures, with phenanthroline. From previous studies of the reactions between the noble metal chlorides and nitron, we knew that insoluble compounds of definite composition were only obtained in the presence of excess of thiocyanate. Surprisingly, many compounds were quantitatively obtained from the critical points of the different heterometric curves.

It would be impossible to discuss here in detail the structures of the many intermediate compounds cited in the tables; attention will be given mainly to the final (= $\downarrow\downarrow$) compounds derived from the titration curves. Their structural presentation seems to be complex, and may depend on the working conditions.

At different compositions of the analysed solutions, six different *final* compounds were obtained at the first maximum optical density points of the curves. Each of these compounds could be used with almost equal success for the determination of the metals. The error obtained was 1% or less. A parallel study was carried out with papaverine, which contains only one nitrogen atom in the closed rings. The reactions of the noble metals with papaverine were about four times as sensitive as those with phenanthroline. In almost all cases, one final compound, $MePv_2$, was obtained with papaverine. The many compounds obtained with phenanthroline could hardly be traced and studied except by heterometry. Apparently the complexes which were formed in the "solid" state were much more varied and interesting than those traced in the homogeneous medium.

EXPERIMENTAL

Reagents

1,10-Phenanthroline (B.D.H. AnalaR) $C_{12}H_8N_2 \cdot H_2O$, was dissolved in water to give a 0.01 *M* stock solution.

Platinum chloride (Johnson, Matthey & Co. Ltd.) ($H_2PtCl_6 \cdot xH_2O$), about 40% platinum. 1 g was dissolved in 250 ml water (approx. 0.008 *M*).

Palladium chloride (Johnson, Matthey & Co. Ltd.) 1 g was dissolved in 250 ml 0.2 *N* HCl (approx. 0.022 *M* $PdCl_2$/0.2 *N* HCl).

Gold chloride (brown) (B.D.H. Laboratory reagent) 1 g of $HAuCl_4 \cdot 3H_2O$ and 25 ml of *N* HCl were dissolved in 250 ml of aqueous solution (approx. 0.01 *M* $HAuCl_4$/0.1 *N* HCl).

Technique

The same apparatus and technique were used as in previous investigations[2]. The reaction temperature was always 20°.

RESULTS

1. *Reactions with chloroplatinic acid*

Table I presents titrations carried out at pH values of *ca.* 1 and *ca.* 7 in solutions of chloride or thiocyanate with phenanthroline (P) as titrant. The table also contains

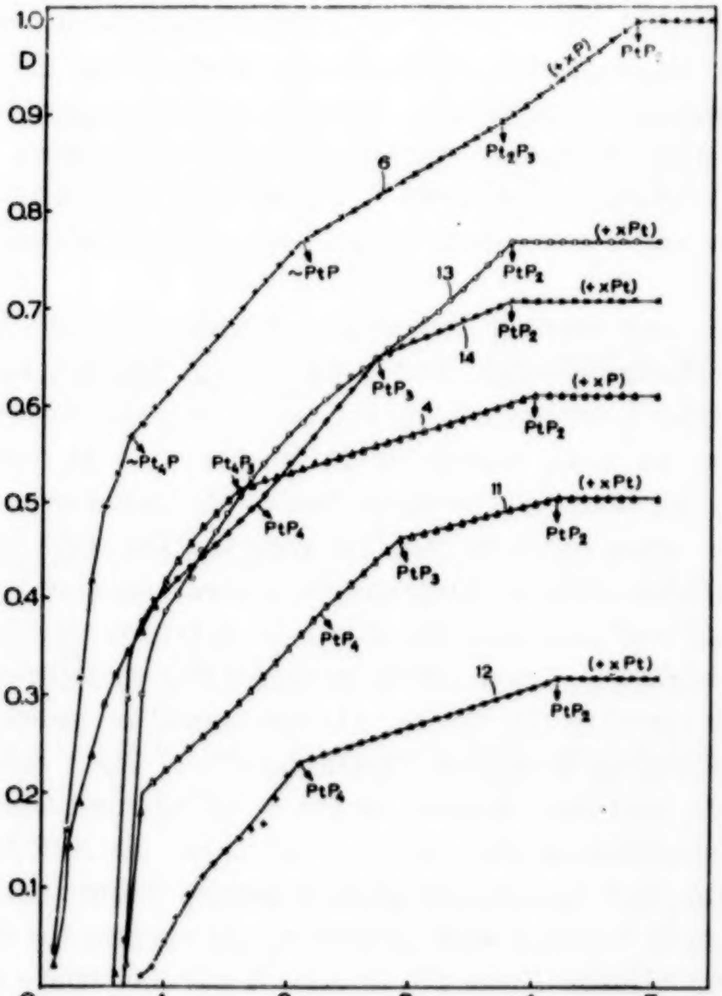


Fig. 1. Titrations of chloroplatinic acid solutions with phenanthroline and the reverse.

a few reverse titrations. The course of some of these experiments is presented in Fig. 1 (the same enumeration is used in the tables and in the corresponding curves). In all cases, if no precipitation occurred in the direct titration, the same held true for the reverse titration. In the presence of chloride no precipitation of the metal with phenanthroline occurred at either of the above pH (Expts. 1–2 and 7–8). In the presence of thiocyanate precipitation occurred only at pH *ca.* 1. Only one final compound was always obtained in thiocyanate solutions, *i.e.* $Pt_1P_2\downarrow\downarrow$. With phenanthroline as titrant (Expts. 3, 4 and 6), theoretical values were obtained at the end-point which was derived from the intersection of the last part of the titration curve with the horizontal maximum density line. The maximum optical density seemed to decrease if too much thiocyanate was present (Expts. 3–4 and 11–12), although the same compound was always quantitatively obtained. A series of intermediate compounds were also obtained; these varied according to the direction of the titration. When phenanthroline was titrated with platinum solution, the following intermediates were obtained:

$$Pt_1P_4\downarrow \xrightarrow{+\ Pt} Pt_1P_3\downarrow \xrightarrow{+\ Pt} PtP_2\downarrow\downarrow$$

This indicates that as many as four phenanthroline molecules can somehow be bound to one atom of platinum. In spite of this, the final compound always showed the same empirical composition, namely $Pt_1P_2\downarrow\downarrow$. The sensitivity of the reaction with platinum was low, so that about 4 mg of platinum were necessary for a titration. The titration time was always 20–30 min, *i.e.* about 2–3 times more than for a corresponding titration of the metal-thiocyanate solution with nitron. The extended time may be

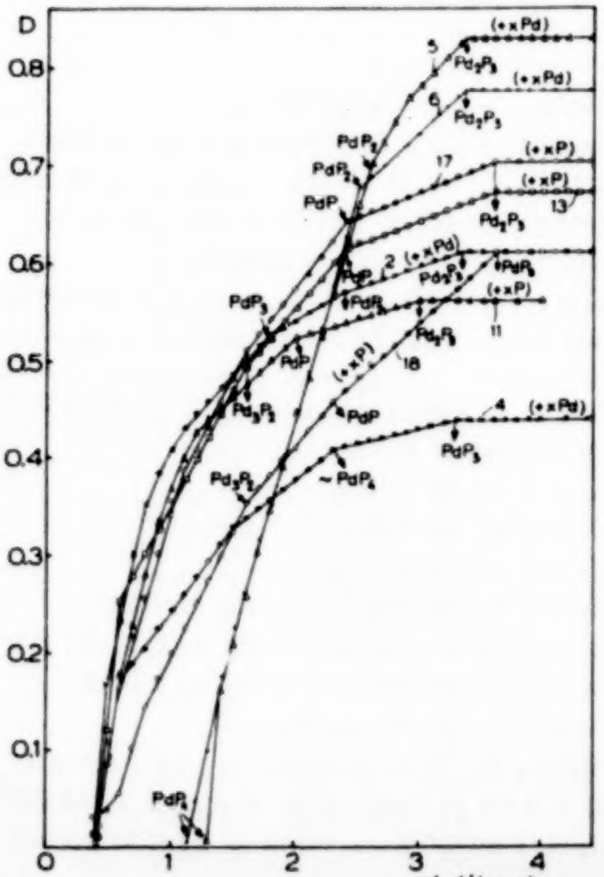


Fig. 2. Titrations of palladium chloride solutions with phenanthroline and the reverse.

TABLE I

General composition: *a* ml reagents

Expt. No.	*Solution titrated*	*Titrant*		*Titration time in min*
		Name	*Molarity*	
1	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3	Phenanthr.	0.01	
2	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml M NaCl	Phenanthr.	0.01	
3	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	Phenanthr.	0.01	21
4	5 ml 0.004 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 2 M KCNS	Phenanthr.	0.01	21
5	3 ml 0.008 M H_2PtCl_6 + 1 ml M HNO_3	Phenanthr.	0.01	
6	3 ml 0.008 M H_2PtCl_6 + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	Phenanthr.	0.01	26
7	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate	Phenanthr.	0.01	
8	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml M NaCl	Phenanthr.	0.01	
9	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml 0.5 M KCNS	Phenanthr.	0.01	
10	3 ml 0.008 M H_2PtCl_6 + 1 ml M Na-acetate + 2 ml 2 M KCNS	Phenanthr.	0.01	
11	5 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.006	20
12	5 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	H_2PtCl_6	0.006	30
13	6 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	H_2PtCl_6	0.008	19
14	6 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	H_2PtCl_6	0.008	18

P = phenanthroline; h = horizontal max. density line; i = intersection point; c = contact point.

TABLE II

General composition: *a* ml reagents

Expt. No.	*Solution titrated*	*Titrant*		*Titration time in min*
		Name	*Molarity*	
1	4 ml 0.005 M phenanthr. + 1 ml M HNO_3	$PdCl_2$	0.004	25
2	4 ml 0.005 M phenanthr. + 1 ml M HNO_3 + 2 ml M NaCl	$PdCl_2$	0.004	36
3	4 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	$PdCl_2$	0.004	38
4	4 ml 0.01 M phenanthr. + 1 ml M HNO_3 + 2 ml M KCNS	$PdCl_2$	0.004	35
5	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate	$PdCl_2$	0.004	30
6	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml M NaCl	$PdCl_2$	0.004	36
7	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml 0.25 M KCNS	$PdCl_2$	0.004	30
8	4 ml 0.005 M phenanthr. + 1 ml M Na-acetate + 2 ml M KCNS	$PdCl_2$	0.004	35
9	3 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	25
10	4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr	0.005	33
11	5 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	32
12	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3	Phenanthr.	0.005	35
13	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M NaCl	Phenanthr.	0.005	32
14	4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	Phenanthr.	0.005	38
15	6 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M KCNS	Phenanthr.	0.01	34
16	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate	Phenanthr.	0.005	30
17	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml M NaCl	Phenanthr.	0.005	32
18	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml 0.25 M KCNS	Phenanthr.	0.005	28
19	6 ml 0.002 M $PdCl_2$ + 1 ml M Na-acetate + 2 ml M KCNS	Phenanthr.	0.005	32

P = phenanthroline; h = horizontal max. density line; c = contact point; i = intersection point; x =

+ (10 — *a*) ml H_2O + *x* ml titrant. T = 20°

TABLE I

ml titrant used at the			*Calculated molar ratios [Pt] : [P]*	*Max. density value*	*% Error*
Init. ppt. point (=↑)	*Intermediate intersection points (=↓)*	*End-point (=↓↓)*			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
0.2	c. 1.45; i 2.55	i 4.00 h	4:3 ↓ → 4:5 ↓ → 1:2 ↓↓	0.95	0.0
0.1	0.5 ; c 1.6	i 4.00 h	4:3 ↓ → 1:2 ↓↓	0.61	0.0
	no ppt.	> 5.0			
0.1	c 0.65; i 2.1; i 3.6	4.80	<4:1↓ → 1:1↓ → 2:3↓ → 1:2↓↓	0.99	0.0
	no ppt.	> 5.0			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
	no ppt.	> 5.0			
0.7	i 2.25; i 2.9	i 4.20 h	1:4 ↓ → 1:3 ↓ → 1:2 ↓↓	0.51	0.8
~ 0.8	~ i 2.0	i 4.20 h	1:4 ↓ → 1:2 ↓↓	0.32	0.8
0.7		i 3.80 h	1:2 ↓↓	0.77	1.3
0.6	1.8; c 2.7	i 3.80 h	1:4 ↓ → ~ 1:3 ↓ → 1:2 ↓↓	0.71	1.3

+ (10 — *a*) ml H_2O + *x* ml titrant. T = 20°

TABLE II

ml titrant used at the			*Calculated molar ratios [Pd] : [P]*	*Max. density value*	*% Error*
Init. ppt. point (=↑)	*Intermediate intersection points (=↓)*	*End-point (=↓↓)*			
0.3	c 1.0; 1.7; 2.5	i 3.30 h	1:5↓ → 1:3↓ → 1:2↓ → 2:3↓↓	0.63	1.2
0.4	c 1.1; 1.8; 2.4	i 3.35 h	1:4↓ → 1:3↓ → 1:2↓ → 2:3↓↓	0.61	0.3
0.4	i 2.4	i 3.30 h	1:4↓ → 1:3↓↓	x 0.54	1.2
0.3	1.5; 2.3	i 3.30 h	1:4↓ → 1:3↓↓	x 0.44	1.2
1.3	2.55; 2.9	i 3.35 h	1:4↑ → 1:2↓ → 3:5↓ → 2:3↓↓	0.82	0.3
1.2	2.5	i 3.35 h	1:4↑ → 1:2↓ → 2:3↓↓	0.77	0.3
0.1	c 1.1	i 3.30 h	~1:5↓ → 2:3↓↓	x 0.79	1.2
0.1	1.0; 1.7	i 3.30 h	1:4↓ → 1:3↓ → 2:3↓↓	x 0.46	1.2
0.5		i 1.8 h	2:3↓↓	0.47	
0.5	0.9; 1.45	i 2.40 h	2:1↓ → 1:1↓ → 2:3↓↓	0.45	0.0
0.4	1.2; 2.00	i 3.00 h	~2:1↓ → 1:1↓ → 2:3↓↓	0.56	0.0
0.4	1.6; 2.4	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.68	0.0
0.4	1.6; 2.40	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.67	0.0
0.6	1.3	i 4.85 h	1:3↓↓	x 0.44	1.0
0.5	(2.0); 2.60	i 3.60 h	~ 1:2↓ → 1:3↓↓	x 0.42	0.0
0.3	1.6; 2.4	i 3.60 h	3:2↓ → 1:1↓ → 2:3↓↓	0.72	0.0
0.4	(1.1); (1.6); 2.4	i 3.60 h	~2:1↓ → 3:2↓ → 1:1↓ → 2:3↓↓	0.70	0.0
0.4	1.6; 2.30	i 3.62 h	3:2↓ → 1:1↓ → 2:3↓↓	x 0.61	0.6
0.3	2.5	i 3.60 h	1:1↓ → 2:3↓↓	x 0.70	0.0

orange Corning filter No. 3484.

explained by the formation of phenanthroline metal-thiocyanate co-ordinated compounds rather than by a normal cation–anion reaction.

2. *Reactions with palladium chloride*

Table II presents a series of titrations of palladium halide solutions with phenanthroline, and *vice versa* at pH values of *ca.* 1 and *ca.* 7. The course of some titrations is presented in Fig. 2. In all cases precipitation occurred. Final compounds of strictly stoichiometric compositions were always obtained at the first maximum density points, after which a horizontal maximum line was obtained. Either the palladium or the phenanthroline could be determined from these points; the error was generally 0–1 %. The titrations in thiocyanate solutions were carried out with an orange filter. Apparently the same final compound was obtained in all titrations with chloride (Pd_2P_3 ↓↓). At *ca.* pH 7 in the presence of excess thiocyanate, a similar compound was obtained (Expts. 16–19). This applies also to the intermediate compounds obtained. On the other hand, if the titrations were carried out at *ca.* pH 1

TABLE III

General composition: *a* ml reager

Expt. No.	*Solution titrated*	*Titrant* *Name*	*Titrant* *Molarity*	*Titratio time in min*
1	4 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3	$AuCl_3$	0.005	25
2	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3	$AuCl_3$	0.005	25
3	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3 + 2 ml *M* NaCl	$AuCl_3$	0.005	22
4	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3 + 1 ml 0.5 *M* NaCl	$AuCl_3$	0.005	25
5	4 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	$AuCl_3$	0.005	19
6	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3 + 2 ml 0.25 *M* KCNS	$AuCl_3$	0.005	20
7	3 ml 0.005 *M* phenanthr. + 0.5 ml *M* HNO_3 + 2 ml *M* KCNS	$AuCl_3$	0.005	25
8	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	$AuCl_3$	0.005	24
9	3 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	$AuCl_3$	0.005	16
9a	2 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate	$AuCl_3$	0.005	24
10	2 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml *M* NaCl	$AuCl_3$	0.005	25
11	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	$AuCl_3$	0.005	17
12	3 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	$AuCl_3$	0.005	18
13	4 ml 0.005 *M* phenanthr. + 1 ml *M* Na-acetate + 2 ml *M* KCNS	$AuCl_3$	0.005	18
14	4 ml 0.005 *M* $AuCl_3$ + 1 ml 0.5 *M* HNO_3	Phenanthr.	0.005	20
15	4 ml 0.005 *M* $AuCl_3$ + 1 ml 0.5 *M* HNO_3 + 2 ml *M* NaCl	Phenanthr.	0.005	23
16	5 ml 0.005 *M* $AuCl_3$ + 1 ml 0.5 *M* HNO_3 + 2 ml 0.25 *M* KCNS	Phenanthr.	0.005	20
17	5 ml 0.005 *M* $AuCl_3$ + 1 ml 0.5 *M* HNO_3 + 2 ml *M* KCNS	Phenanthr.	0.005	26
18	4 ml 0.005 *M* $AuCl_3$ + 1 ml *M* Na-acetate	Phenanthr.	0.005	20
19	4 ml 0.005 *M* $AuCl_3$ + 1 ml *M* Na-acetate + 2 ml *M* NaCl	Phenanthr.	0.005	21
20	4 ml 0.005 *M* $AuCl_3$ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	Phenanthr.	0.01	21
21	4 ml 0.005 *M* $AuCl_3$ + 1 ml *M* Na-acetate + 2 ml 0.25 *M* KCNS	Phenanthr.	0.01	20

P = phenanthroline; i = intersection point; h = horizontal max. density line; l.i. = linear increase aft in the presence of potassium thiocyanate, the composition of the final compound was Pd_1P_3 ↓↓ instead of Pd_2P_3 ↓↓.

For these determinations, approximately one mg of palladium was necessary. The titration time was extended to 30–40 min, *i.e.* about 3–4 times longer than with nitron. (Extended titration times were also observed in similar reactions with papaverine). Again time was needed for the formation of the phenanthroline–palladium complex at room temperature. From the analytical aspect, the use of thiocyanate for chloride had no advantage. There was little difference in the results whether a coloured filter was used or not.

3. *Reactions with gold chloride*

Table III presents a selection of experiments of titrations of gold chloride solutions with phenanthroline and *vice versa* (see also Fig. 3). The reaction with gold has approximately the same sensitivity as that of platinum. Both the chloride and the thiocyanate solutions were tested. The empirical compositions of the final compounds

(10 — a) ml H_2O + x ml titrant. T = 20° TABLE III

ml titrant used at the			Max. density value	Calculated molar ratios [Au] : [P]	% Error
Init. ppt. point (=↑)	Intermediate intersection points (=↓)	End-point (=↓↓)			
1.3	1.8	i 4.00 h	0.79	1:3↑ →1:2↓ →1:1↓↓	0.0
2.0	2.3	i 3.00 h	0.49	2:3↑ →4:5↓ →1:1↓↓	0.0
1.5	2.2	i 3.00 h	0.29	1:2↑ →3:4↓ →1:1↓↓	0.0
1.2	2.03	i 3.00 h	0.40	2:5↑ →2:3↓ →1:1↓↓	0.0
0.2	2.1; 2.9	i 4.00 h	x 0.75	1:2↓ →3:4↓ →1:1↓↓	0.0
0.2	2.0	i 3.00 l.i.	xx 0.54	2:3↓ → 1:1↓↓	0.0
1.9	2.3	i 3.00 h	x 0.51	2:3↑ →3:4↓ →1:1↓↓	0.0
3.6				~1:1↑	
2.5		c 3.00 l.i.	0.51	4:5↑ → 1:1↓	
1.3		4.00 h	0.58	2:3↑ → 2:1↓↓	0.0
0.8	1.5; 2.2	i 4.00 h	0.51	2:3↑ →~1:1↓ →2:1↓↓	0.0
0.1	1.56	i 2.00 h	x 0.80	1:2↓↓	0.0
0.6	(1.1)	i 1.50 h	0.62	(1:3)↑ → 1:2↓↓	0.0
0.35	(1.05); c. 1.4	i 2.00 h	x 0.57	(1:4)↑ →1:3↓ → 1:2↓↓	0.0
1.0	2.35	i 4.00 h	0.55	4:1↑ →~3:2↓ → 1:1↓↓	0.0
1.0	1.4; 2.3	i 4.00 h	0.43	4:1↑ →3:1↓ →~3:2↓ →1:1↓↓	0.0
0.6	0.8; 1.2	i 2.50 h	x 0.41	5:1↓ →4:1↓ → 2:1↓↓	0.0
0.5	1.37	2.50 h	x 0.41	<4:1↓ → 2:1↓↓	0.0
0.6	0.9; 1.5	i 2.00 h	0.58	4:1↓ →~3:1↓ → 2:1↓↓	0.0
0.7	1.2	i 2.00 h	0.55	~4:1↓ → 2:1↓↓	0.0
0.5	1.2; 2.0; 2.8	i 4.00 h	0.64	~2:1↓ →1:1↓ →2:3↓ →1:2↓↓	0.0
0.6	2.8	i 4.00 h	x 0.54	2:3↓ →1:2↓↓	0.0

he end-point; c = contact point; x = orange Corning filter No. 3484; xx = yellow Corning filter No. 3385.

obtained partly depended on the pH value of the solution and on whether the phenanthroline or the gold chloride was used as titrant. Thus, at pH *ca.* 1, if gold chloride was used as titrant (Expts. 1–7), the composition of the final compound was AuP ↓↓ with both chloride and thiocyanate. At pH *ca.* 7, the results were different: in chloride solution Au_2P ↓↓ was obtained (Expts. 9a and 10), while in thiocyanate solution (Expts. 11–13) AuP_2 ↓↓ was obtained. With phenanthroline as titrant, we obtained AuP ↓↓ at pH *ca.* 1 with chloride (Expts. 14 and 15), and Au_2P ↓↓ with thiocyanate (Expts. 16 and 17). At pH *ca.* 7, we obtained Au_2P ↓↓ with chloride (Expts. 18 and 19), while with thiocyanate, AuP_2 ↓↓ (Expts. 20 and 21). The sensitivity of the reaction, *i.e.* the maximum density value obtained for a given quantity of gold, was only slightly dependent on the composition of the final compound (Expts. 16, 17, 20 and 21). The results were not improved by the use of a filter (Expts. 20 and 21). At the point of the initial precipitation, the following intermediate compounds were obtained in solution: AuP_3 (Expt. 12), when titrated with gold, and Au_4P ↑ when titrated with phenanthroline (Expt. 15). The titration time was 20–30 min.

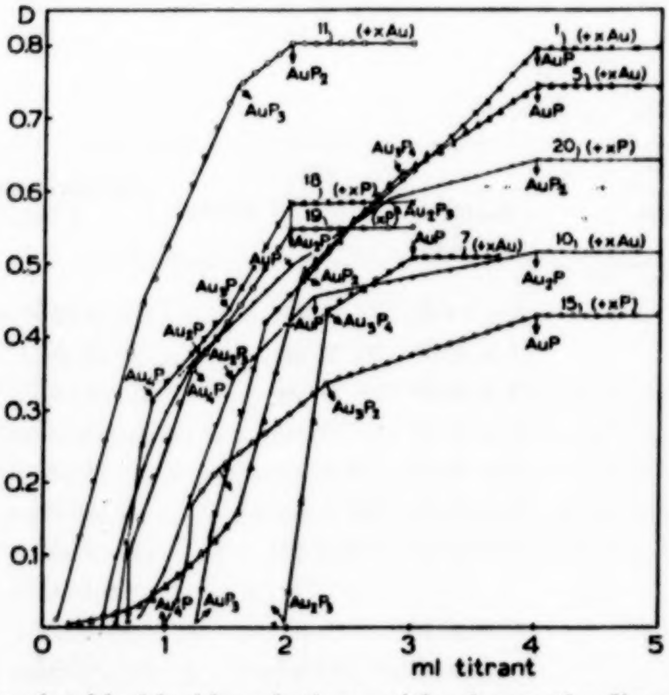


Fig. 3. Titrations of gold chloride solutions with phenanthroline and the reverse.

TABLE IV

H_2PtCl_6				*$PdCl_2$*				*$HAuCl_4$*			
Titrant	*pH*	*R^-*	*Compound*	*Titrant*	*pH*	*R^-*	*Compound*	*Titrant*	*pH*	*R^-*	*Compound*
phenanthr.	1	Cl^-	soluble	phenanthr.	1	Cl^-	Pd_2P_3↓↓	phenanthr.	1	Cl^-	Au_1P_1↓↓
phenanthr.	7	Cl^-	soluble	phenanthr.	7	Cl^-	Pd_2P_3↓↓	phenanthr.	7	Cl^-	Au_2P_1↓↓
phenanthr.	1	CNS^-	Pt_1P_2↓↓	phenanthr.	1	CNS^-	Pd_1P_3↓↓	phenanthr.	1	CNS^-	Au_2P_1↓↓
phenanthr.	7	CNS^-	soluble	phenanthr.	7	CNS^-	Pd_2P_3↓↓	phenanthr.	7	CNS^-	Au_1P_2↓↓
H_2PtCl_6	1	Cl^-	soluble	$PdCl_2$	1	Cl^-	Pd_2P_3↓↓	$HAuCl_4$	1	Cl^-	Au_1P_1↓↓
H_2PtCl_6	7	Cl^-	soluble	$PdCl_2$	7	Cl^-	Pd_2P_3↓↓	$HAuCl_4$	7	Cl^-	Au_2P_1↓↓
H_2PtCl_6	1	CNS^-	Pt_1P_2↓↓	$PdCl_2$	1	CNS^-	Pd_1P_3↓↓	$HAuCl_4$	1	CNS^-	Au_1P_1↓↓
H_2PtCl_6	7	CNS^-	soluble	$PdCl_2$	7	CNS^-	Pd_2P_3↓↓	$HAuCl_4$	7	CNS^-	Au_1P_2↓↓

DISCUSSION

The reactions of noble metal halides with phenanthroline are interesting because of the variety of the final compounds which were stoichiometrically and quantitatively obtained at the first maximum optical density points. A further report will show that this presents special advantages for the determination of the metals in alloys or in a soluble mixture of chlorides of all the three metals concerned. The working conditions can be varied very easily.

The present paper deals with the most probable structures of the different, and especially the final, compounds obtained. In each case, the sequence of intermediates which led to the final compound are also considered. Table IV lists the working conditions under which each of the final compounds was obtained.

It is interesting to note that the only palladium compound, $PdC_{12}H_8N_2Cl_2$, which has been used for the gravimetric determination of palladium, does not appear in our experiments as a final compound, but only as an intermediate. The following presentation indicates reasonable structures for the compounds obtained.

Platinum compounds

If platinum chloride was titrated with phenanthroline at *ca.* pH 1 in thiocyanate solution, or *vice versa*, (Table I, Expts. 1–6 and 11–14), the following two sequences of intermediates and final compounds were derived from the curves:

$$\frac{> \mathrm{Pt} + x\mathrm{P}}{(\mathrm{pH} \sim 1)} : (\mathrm{Pt_4P}\downarrow) \rightarrow \mathrm{PtP}\downarrow \rightarrow \mathrm{Pt_2P_3}\downarrow \rightarrow \mathrm{PtP_2(CNS)_4}\downarrow\downarrow \tag{1}$$

$$\frac{> \mathrm{P} + x\mathrm{Pt}}{(\mathrm{pH} \sim 1)} ; \mathrm{PtP_4}\downarrow \rightarrow \mathrm{PtP_3}\downarrow \rightarrow \mathrm{PtP_2(CNS)_4}\downarrow\downarrow \tag{2}$$

Palladium compounds

If palladium chloride was titrated at pH values 1–7 with phenanthroline, or *vice versa*, the same empirical final compound was always obtained, namely $Pd_2P_3Cl_4\downarrow\downarrow$. If thiocyanate was present in sufficient excess, two compounds were obtained. At *ca.* pH 1 the empirical composition of the final compound was $PdP_3(CNS)_2\downarrow\downarrow$, but at *ca.* pH 7 the final compound was $Pd_2P_3(CNS)_4\downarrow\downarrow$. The following sequences of intermediates and final compounds were obtained:

$$\frac{> \mathrm{Pd} + x\mathrm{P}}{(\mathrm{pH's}\ 1\text{–}7)} : \mathrm{Pd_2P_1}\downarrow \rightarrow \mathrm{Pd_3P_2}\downarrow \rightarrow \mathrm{PdP}\downarrow \rightarrow \mathrm{Pd_2P_3Cl_4}\downarrow\downarrow \tag{3}$$

$$\frac{> \mathrm{P} + x\mathrm{Pd}}{(\mathrm{pH's}\ 1\text{–}7)} : \mathrm{PdP_4}\uparrow\downarrow \rightarrow \mathrm{PdP_3}\downarrow \rightarrow \mathrm{PdP_2}\downarrow \rightarrow \mathrm{Pd_2P_3Cl_4}\downarrow\downarrow \tag{4}$$

$$\frac{> \mathrm{Pd} + x\mathrm{P}}{(\mathrm{pH} \sim 1)} : \mathrm{PdP_2}\downarrow \rightarrow \mathrm{PdP_3(CNS)_2}\downarrow\downarrow \tag{5}$$

$$\frac{> \mathrm{Pd} + x\mathrm{P}}{(\mathrm{pH} \sim 7)} : (\mathrm{Pd_3P_2}\downarrow) \rightarrow \mathrm{PdP}\downarrow \rightarrow \mathrm{Pd_2P_3(CNS)_4}\downarrow\downarrow \tag{6}$$

$$\frac{> \mathrm{P} + x\mathrm{Pd}}{(\mathrm{pH} \sim 1)} : \mathrm{PdP_4}\downarrow \rightarrow \mathrm{PdP_3(CNS)_2}\downarrow\downarrow \tag{7}$$

$$\frac{> \mathrm{P} + x\mathrm{Pd}}{(\mathrm{pH} \sim 7)} : \mathrm{PdP_4}\downarrow \rightarrow \mathrm{PdP_3}\downarrow \rightarrow \mathrm{Pd_2P_3(CNS)_4}\downarrow\downarrow \tag{8}$$

Gold compounds

Three different final compounds were obtained with gold chloride in chloride or thiocyanate solutions, namely $\mathrm{AuP_2}\downarrow\downarrow$, $\mathrm{AuP}\downarrow\downarrow$ and $\mathrm{Au_2P}\downarrow\downarrow$. In the chloride solution at *ca.* pH 1 the final compound $\mathrm{AuPCl_3}\downarrow\downarrow$ was always obtained; at *ca.* pH 7 $\mathrm{Au_2PCl_6}\downarrow\downarrow$ was obtained.

In thiocyanate solution at *ca.* pH 1 two final compounds were obtained. If $\mathrm{AuCl_3}$ was used as titrant, the compound was $\mathrm{AuP(CNS)_3}\downarrow\downarrow$, but in the reverse case $\mathrm{Au_2P(CNS)_6}\downarrow\downarrow$ was formed. At *ca.* pH 7 both types of titrations gave the same final compound, $\mathrm{AuP_2(CNS)_3}\downarrow\downarrow$.

The following sequences of intermediates and final compounds were obtained:

$$\frac{> \mathrm{Au} + x\mathrm{P}}{(\mathrm{pH} \sim 1)} : \mathrm{Au_4P}\downarrow \rightarrow \mathrm{Au_3P}\downarrow \rightarrow \mathrm{Au_3P_2}\downarrow \rightarrow \mathrm{AuPCl_3}\downarrow\downarrow \tag{9}$$

$$\frac{> \mathrm{Au} + x\mathrm{P}}{(\mathrm{pH} \sim 7)} : \mathrm{Au_4P}\downarrow \rightarrow \mathrm{Au_3P}\downarrow \rightarrow \mathrm{Au_2PCl_6}\downarrow\downarrow \tag{10}$$

$$\frac{> \mathrm{P} + x\mathrm{Au}}{(\mathrm{pH} \sim 1)} : (\mathrm{AuP_3})\uparrow \rightarrow \mathrm{AuP_2}\uparrow\downarrow \ldots \mathrm{AuPCl_3}\downarrow\downarrow \tag{11}$$

$$\frac{> \mathrm{P} + x\mathrm{Au}}{(\mathrm{pH} \sim 7)} : \mathrm{Au_2P_3}\uparrow \rightarrow \mathrm{AuP}\downarrow \rightarrow \mathrm{Au_2PCl_6}\downarrow\downarrow \tag{12}$$

$$\frac{> \mathrm{P} + x\mathrm{Au}}{(\mathrm{pH} \sim 1)} : \mathrm{AuP_2}\downarrow \rightarrow \mathrm{Au_2P_3}\downarrow \rightarrow (\mathrm{Au_3P_4}\downarrow) \rightarrow \mathrm{AuP(CNS)_3}\downarrow\downarrow. \tag{13}$$

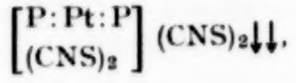
$$\frac{> \mathrm{P} + x\mathrm{Au}}{(\mathrm{pH} \sim 7)} : (\mathrm{AuP_4}\downarrow) \rightarrow \mathrm{AuP_3}\downarrow \rightarrow \mathrm{AuP_2(CNS)_3}\downarrow\downarrow \tag{14}$$

$$\frac{> \mathrm{Au} + x\mathrm{P}}{(\mathrm{pH} \sim 1)} : \mathrm{Au_4P}\uparrow \rightarrow \mathrm{Au_2P(CNS)_6}\downarrow\downarrow \tag{15}$$

$$\frac{> \mathrm{Au} + x\mathrm{P}}{(\mathrm{pH} \sim 7)} : \mathrm{Au_2P}\downarrow \rightarrow \mathrm{AuP}\downarrow \rightarrow \mathrm{Au_2P_3}\downarrow \rightarrow \mathrm{AuP_2(CNS)_3}\downarrow\downarrow \tag{16}$$

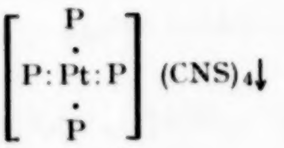
One of us (M.B.) is preparing a special report dealing with the structures of nitrogen compounds with the noble metal halides. Therefore only a few structures, mostly of final compounds are presented here.

Thus, the $\mathrm{PtP_2(CNS)_4}\downarrow\downarrow$ in equations (1) and (2) probably has the structure



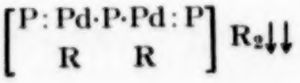
$$\left[\begin{matrix}\mathrm{P:Pt:P} \\ \mathrm{(CNS)_2}\end{matrix}\right]\mathrm{(CNS)_2}\downarrow\downarrow.$$

while the primary intermediate compound in equation (2) may have the structure



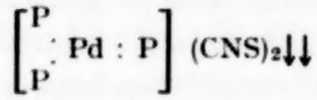
$$\left[\begin{matrix} & \mathrm{P} & \\ & \cdot & \\ \mathrm{P:} & \mathrm{Pt} & \mathrm{:P} \\ & \cdot & \\ & \mathrm{P} & \end{matrix}\right]\mathrm{(CNS)_4}\downarrow$$

The final palladium compound $\mathrm{Pd_2P_3R_4}\downarrow\downarrow$ in equations (3), (4), (6) and (8) may be represented as:



$$\left[\begin{matrix}\mathrm{P:Pd\cdot P\cdot Pd:P} \\ \mathrm{R}\qquad\mathrm{R}\end{matrix}\right]\mathrm{R_2}\downarrow\downarrow$$

while the compound $PdP_3(CNS)_2 \downarrow\downarrow$ in equation (5) may have the structure:



$$\left[\begin{matrix} P & & \\ \vdots & Pd : P \\ P & & \end{matrix}\right] (CNS)_2\downarrow\downarrow$$

The following may be stated regarding the gold compounds obtained: $AuPR_3 \downarrow\downarrow$, obtained in equations (9), (11) and (13), may be shown as: $[R_2Au : P]R \downarrow\downarrow$.

$Au_2PR_6 \downarrow\downarrow$ in equations (10), (12) and (15) may be shown as the salt complexes: $[P : AuR_2]\,[AuR_4] \downarrow\downarrow$, $[P : Au : P]\,[AuR_4]_3 \downarrow\downarrow$ or as a complex compound: $R_3Au.P.AuR_3 \downarrow\downarrow$. The formation of one or the other depends on the pH value, on the titrant used, and on the halide participating in the complex formation. The compound $AuP_2(CNS)_3 \downarrow\downarrow$ was obtained at pH 7 only (eqn. 14 and 16) and may be represented as: $[P : Au : P]\,(CNS)_3 \downarrow\downarrow$.

SUMMARY

The reactions between platinum, palladium and gold halides and phenanthroline were studied heterometrically. By changing the composition of the solutions, six different final compounds were obtained. Each of the compounds could be used for the determinations of the metals. The errors were one per cent or less. The most probable structural formulae for the final compounds are presented.

RÉSUMÉ

Les auteurs ont effectué une étude hétérométrique des réactions et des composés obtenus entre les halogénures de platine, de palladium et d'or, et la phénanthroline. Chacune de ces réactions peut servir au dosage de ces trois métaux.

ZUSAMMENFASSUNG

Die Reaktionen zwischen Platin-, Palladium- und Goldchlorid und Phenanthrolin sowie die Zusammensetzung der Reaktionsprodukte wurden heterometrisch untersucht. Diese Reaktionen können zur Bestimmung der drei Metalle verwendet werden.

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Short Communications

The behaviour of pyro- and tripoly-phosphate complexes at the dropping mercury electrode

Whether or not covalent bonding as well as electrostatic attraction plays a part in the stabilization of the metal complexes of straight chain polyphosphates[1], the close structural similarity between pyrophosphate and tripolyphosphate ions should result in their metal complexes having similar properties. A study of their behaviour at the dropping mercury electrode is therefore of interest. Some of the preliminary data obtained in this connection are reported below.

The half-wave potentials for the cathodic waves of a few metals obtained in aqueous pyrophosphate and tripolyphosphate media are given in Table I (literature values for the half-wave potentials of the simple metal ions in solution are included for comparison). All the metals give single steps which are well-developed and free from maxima. For a given metal, the resemblance between the two waves in the two phosphate media is striking. The diffusion plateau for the niobium step in either phosphate is somewhat masked by the discharge of the supporting electrolyte. Separation of the niobium step from the final current rise is, however, obtained in the derivative polarogram ($E_{d.e}$ *vs.* $di/dE_{d.e}$). At pH 5 the wave for lead is reversible in both the phosphates. Waves for the other metals listed in Table I (including those for lead at pH 7) are all irreversible. Reversible waves in pyrophosphate media have been reported[2,3] for a few metals but the waves become irreversible at higher pH. Very few data are available for waves in tripolyphosphate media[4].

Half-wave potentials of irreversible steps cannot of course be directly correlated to the dissociation constants of the complexes, but they qualitatively reflect the relative stabilities. It may be observed from Table I that the differences in the half-wave potentials between the simple metal ions, lead, bismuth, titanium, and their respective complexes are slightly more for the tripolyphosphate complex than for the pyrophosphate complex. This is in accord with the generally observed fact that the stability of a complex formed with a chain phosphate increases with the number of phosphorus atoms in the chain.

TABLE I

REDUCTION OF PYRO- AND TRIPOLY-PHOSPHATE COMPLEXES AT THE DROPPING MERCURY ELECTRODE

Electrolyte composition: 0.5 m*M* depolarizer under test, 0.1 *M* sodium pyro- or tripoly-phosphate, ionic strength adjusted to 1.2 with sodium perchlorate. T = 30° ± 1°

Depolarizer	*pH*	*Buffer*	$E_{\frac{1}{2}}$ *vs. S.C.E. in V in pyrophosphate*	$E_{\frac{1}{2}}$ *vs. S.C.E. in V in tripolyphosphate*	$E_{\frac{1}{2}}$ *vs. S.C.E. in V for simple metal ions*
Pb^{+2}	5	Phthalate	—0.485	—0.524	—0.38 (1 *M* $HClO_4$)
	7	Phosphate	—0.580	—0.605	
Bi^{+3}	5	Acetate	—0.277	—0.344	+0.02 (0.7 *M* $HClO_4$)
	7	Phosphate	—0.589	—0.685	
Ti^{+4}	2		—0.372	—0.316	—0.81 (0.1 *N* HCl)
Nb^{+5}	7	Unbuffered	*ca.* —1.6	*ca.* —1.6	—0.455 (conc. HCl)

In the case of Nb^{+5}, the tripolyphosphate concentration was 0.2 *M* and consequently the ionic strength was higher

Surface-active materials which are strongly adsorbed on the mercury drop tend to retard or suppress these waves[4]. For example, when 0.01% gelatin is added to the base electrolyte, the waves for bismuth, titanium and niobium in both the phosphates are seriously distorted. The effect on the lead wave is less pronounced. Addition of 0.01% camphor displaces these waves to more negative potentials. As a result, the half-wave potentials of lead, bismuth and titanium in both the chain phosphates shift to around —1.0 V. The niobium wave in either phosphate remains unaffected probably because its half-wave potential (*ca.* —1.6 V) is beyond the desorption potential of camphor[5] (*ca.* —1.3 V). Conversely, gelatin, which is not completely desorbed[6] even at the discharge potential of potassium, obliterates the complexed niobium waves. Similar effects of camphor and gelatin on other polarograms have been observed[5,7] by others. It is believed that in such cases adsorption of the depolarizer on the mercury surface is a prerequisite for electro-reduction to occur.

A fuller account of the work will be published shortly.

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Thermal properties of iron(II) ethylenediammonium sulfate

Iron(II) ethylenediammonium sulfate 4-hydrate, $FeSO_4 \cdot (CH_2NH_3)_2SO_4 \cdot 4H_2O$, has been suggested as a primary standard for oxidative titrimetry[1–3] and is commercially available in a highly purified form intended for this purpose. However, a search of the literature does not show that a study has been reported on the thermal stability of this compound.

For the present work, a sample of iron(II) ethylenediammonium sulfate 4-hydrate, primary standard grade, was obtained from the G. Frederick Smith Chemical Co. and subjected to thermogravimetric examination and differential thermal analysis (DTA). The thermobalance and the DTA apparatus have been previously described[4,5].

The thermobalance and DTA thermal decomposition curves of the compound are given in Fig. 1. Using as an example a sample weighing 78.0 mg, curve A in Fig. 1 was obtained. The compound was stable up to 125°, at which point it began to lose water of hydration, the process being completed at 238°. This first weight loss corresponded to the evolution of 4 moles of water per mole of compound as evidenced by the data: water lost, 17.8%; theoretical weight loss for $4H_4O$, 18.0%. It is to be noted that a shoulder occurs at 175°, suggesting that the water is eliminated in two equal steps. Beyond 295°, a further weight loss occurs, terminating at 475°, which corresponds roughly to the loss of $(CH_2NH_3)_2SO_4$. Beyond this temperature, the iron(II) sulfate began to decompose to the oxide, iron(III) oxide; however, the process was not completed. The loss of weight between 295 and 475° is about 10% less than the theoretical value; it is supposed that this is caused by the oxidation of some of the $FeSO_4$ to the oxide.

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The DTA thermal decomposition curve of the compound is shown in curve B of Fig. 1. Two well-defined endotherms are present at 140° and 210°, which corresponds to the loss of the hydrate water. The other peaks obtained do not lend themselves to easy interpretation but do represent the decomposition of the anhydrous compound to iron(III) oxide. The peak maximas are obtained at different temperatures than those found on the thermobalance curve because of the different furnace conditions and also heating rates employed.

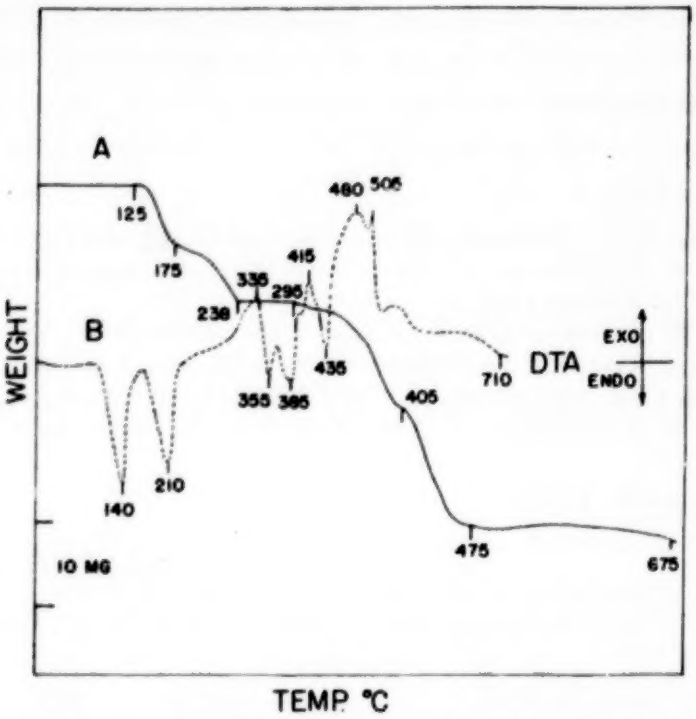

Fig. 1. Thermal decomposition of iron(II) ethylenediammonium sulfate 4-hydrate. Curve A. Thermobalance curve. Curve B. DTA curve.

From the above information, it may be concluded that the iron(II) ethylenediammonium sulfate 4-hydrate can be safely dried at a temperature of 105 to 110° in air without danger of decomposition or oxidation. The anhydrous salt, is stable in the 238 to 295° temperature range, at the heating rate employed.

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BOOK REVIEW

The Analysis of Titanium and its Alloys, 3rd Ed., Imperial Chemical Industries Ltd., The Kynoch Press, Birmingham 1959, Pp. 119. Price 21 s.

Many problems peculiar to nuclear reactors, travel in the atmosphere and in outer space, corrosion, etc. have been satisfactorily solved by using unconventional materials such as titanium, zirconium, beryllium, and their alloys. Until recently, these materials have not been available commercially and there has been a corresponding lack of methods for their analysis published in the scientific literature. This situation was partly remedied by the appearance, in 1956, of the manual "*The Analysis of Titanium and its Alloys*", an outcome of the considerable research carried out by Imperial Chemical Industries (I.C.I.) Ltd. in the field of titanium technology.

Since 1956, further rapid progress in titanium technology has ensured that analytical methods be kept under constant review. Modifications and replacements of earlier procedures, together with methods for determination of additional elements, both as impurities and as alloying constituents, soon appeared in the form of a second edition (1957) of the manual.

Current procedures are contained in the recent third edition, in which the high standard one has grown to expect from all I.C.I. publications, is maintained. Although the layout of previous editions has been preserved, methods of analysis are now presented under 28 different section headings. It is interesting to note from the bibliography that much of the original work has in fact been contributed by I.C.I. itself.

Several procedures appear for the first time in the third edition: absorptiometric determination of boron with curcumin, following preliminary separation of boron by distillation as methyl borate, a simplified low-pressure method for routine determination of carbon, differential absorptiometric determination of alloying amounts of molybdenum, a method not subject to interference from tungsten as is the previously recommended gravimetric procedure using α-benzoinoxime, and absorptiometric determination of low amounts of nitrogen via the sensitive indophenol colour reaction. Turbidimetric determination of small quantities of chlorine has been replaced by a simple, but elegant, amperometric procedure. A feature of the third edition is a statement of the reproducibility attainable with every procedure. In order to readily differentiate between titanium and its alloys, a short section has been added on spot test procedures. A table of atomic numbers and weights has also been included and, in the reviewer's opinion, logarithmic tables might usefully be incorporated into any future edition.

As to be expected from work in a field still so relatively new, several previously recommended procedures have now been modified in the light of further experience. Thus, absorptiometric determination of chromium with diphenylcarbazide has been largely re-written, copper below 0.005% is now determined by means of the chloroform-extractable diethyldithiocarbamate complex instead of with bis-cyclohexanone oxalyldihydrazone, determination of phosphorus below 0.05%, as for higher amounts, is still based on formation of the yellow phospho-vanadomolybdate complex but solvent extraction of the latter with amyl alcohol–ether is recommended, and the "gettering" effects of manganese, when determining oxygen in titanium–manganese alloys by vacuum fusion, has been overcome. The use of high-frequency (R.F.) induction heating of samples in the determination of hydrogen by vacuum extraction, statement of the interference of molybdenum, chromium, nickel and vanadium, in the method for determination of iron and how to overcome this, how to counteract the interference of iron in the absorptiometric determination of nickel, and the need for blanks on tin-free titanium in the determination of tin, are but a few of the more minor modifications to the text of the second edition.

In the section on phosphorus determination, "containing more than 3% manganese" (p. 85) should surely be "less than", while no reference is made to "Note I" in the text detailing flame photometric determination of sodium, although a Note I (p. 92) subsequently follows. These are the only errors which have been detected, the typography being excellent.

Minor criticisms of the text are the need to enlarge on "It is recommended . . . pick-up of boron" (p. 18) and "then remove the oxide layer" (p. 19), while instead of "titrate the chromate" (p. 106) it would be preferable to say "titrate the dichromate", which would be the state of the anion in sulphuric acid solution. Of more importance, however, is the failure to mention precautions for satisfactory weighing of a hygroscopic precipitate such as calcium oxide (p. 22). In any case it would seem better to convert the oxide to carbonate, a more favourable weighing form for calcium. The conversion could hardly prolong the determination since it is recommended that the calcium oxalate precipitate be allowed "to settle for 3–4 hours, preferably overnight". Because of the time already needed to produce a granular precipitate, the technique of homogeneous precipitation might be employed with advantage on this occasion.

The removal of traces of deleterious manganese dioxide, when preparing a standard solution of potassium permanganate (p. 107), could be appreciably quickened, without ill effect, by merely heating the solution at about 90° for one hour, cooling, then filtering through a calcined asbestos pad. Finally, the reviewer would like to see a note in one of the earlier sections of the manual, stressing the need to remove "titanium silicate" stains from beakers, etc. with a suitable solvent as soon as possible after use. Otherwise, the stains may only be removed, if at all, with great difficulty.

In conclusion, for the uninitiated, there are many pitfalls in the specialised field of titanium analysis, inherent difficulties of sampling, use of unconventional solvents, need to avoid hydrolysis when processing titanium solutions, etc. The interested analytical public is, therefore, greatly indebted to I.C.I. for continuing to make available, at a most reasonable price, its wealth of experience in this field. Perhaps it is too much to hope that, eventually, either the manual may be enlarged to include methods for analysis of zirconium, beryllium, and their alloys, or possible even that separate manuals may be published on these subjects.

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Anal. Chim. Acta, 22 (1960) 499–500

REVUE DE LIVRE

The Chemical Society Annual Reports on the Progress of Chemistry for 1958, Vol. LV, Londres 1959, The Chemical Society Burlington House, London, W.1., 527 p. Prix £ 2.0.0.

Nous ne donnerons, dans ce compte rendu, que les chapitres susceptibles d'intéresser directement le chimiste analyste. C'est le cas pour le premier chapitre intitulé: Chimie minérale et chimie physique, qui traitent des progrès réalisés dans le domaine des équilibres acide–base et de la précision des déterminations thermodynamiques des constantes de ces couples en solution, effectuées à partir de la F.E.M., par spectrophotométrie ou par conductibilité. On y trouve aussi un paragraphe sur l'hydrolyse des cations et un autre sur les oxy-acides en solution aqueuse. Enfin, sous le titre de ,,ions association", les auteurs décrivent les principaux travaux effectués sur les liaisons entre ions, sur les propriétés thermodynamiques, sur la conductibilité et sur le comportement dans le visible, dans l'ultra-violet et dans l'infra-rouge, qui en découlent. Un paragraphe est consacré à l'électrochimie.

Dans cet ouvrage, 40 pages seulement sont réservées à la chimie analytique, aussi ne peut-on reprocher aux auteurs de ne donner qu'un bref aperçu des recherches faites dans ce domaine au cours de l'année 1958. Les principales rubriques sont: Généralités analyse qualitative, analyse quantitative inorganique et organique avec comme paragraphes: quantitative (gravimétrique), quantitative (volumétrique). Enfin, les méthodes physico-chimiques sont passées en revue parmi lesquelles la chromatographie, la spectrophotométrie inorganique et organique, la spectrographie, la micro-analyse, les méthodes radiochimiques et l'appareillage. Quelque 60 pages sont consacrées à la chimie inorganique, dont la plus grande partie aux éléments de transition. La chimie organique et la chimie biologique occupent une très vaste place dans ce rapport annuel.

La lecture en est agréable, elle donne un aperçu utile du développement de la chimie au cours de l'année 1958, les faits y sont exposés dans un ordre logique, dans un style concis et clair. Une table des matières et une table des auteurs permettent aux lecteurs de trouver rapidement le sujet qui les intéresse.

D. Monnier (Genève)

Anal. Chim. Acta, 22 (1960) 500

THE ORIGIN OF NUCLEI IN PRECIPITATION REACTIONS

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The purposes of this paper are (a) to present data concerning the origin of nuclei in precipitation reactions and (b) to suggest on the basis of these data and previously published information a mechanism of nucleation which is free of several inconsistencies in other proposed mechanisms.

The classical approach to the physical mechanism of precipitation is based upon the concept of the metastable and labile states of supersaturation[1-3]. As developed and applied to the precipitation of slightly soluble inorganic substances by VON WEIMARN[4] and others, it was concluded that the rate of precipitation and the number of particles are proportional to the degree of supersaturation at the time of precipitation. VON WEIMARN did not clearly distinguish between nucleation and crystal growth, as was promptly emphasized by BANCROFT[5], and many factors other than degree of supersaturation have been found to influence the number of particles. Nevertheless the concept has played a major role in the selection of optimum conditions for analytical precipitation procedures.

Recent approaches to the physical mechanism of nucleation are of two types. One is a theoretical one based upon the work of formation of the nucleus. TURNBULL[6] has developed this concept with particular reference to the nucleation of ionic crystals such as barium sulfate. His conclusions included the following: (a) the rate of nucleation is highly dependent upon the extent of supersaturation, (b) the size of the nucleus is also a function of the degree of supersaturation, and (c) the number of "molecules" or ion pairs is of the order of tens for even the smallest nuclei and likely hundreds for most nuclei.

The other approach to the mechanism of nucleation is based upon the experimental measurement of the induction period, which is the time which elapses between the mixing of reactant solutions and the first detectable appearance of precipitate. CHRISTIANSEN AND NIELSEN[7,8] and others[9-12] have determined the sizes of nuclei from the lengths of the induction periods and obtained, for example, eight ions for barium sulfate, six for silver chromate and nine for calcium fluoride. The experimental methods of measuring the lengths of the induction period may be open to question, but this factor likely would not alter the conclusions that (a) there is a definite critical size of nucleus for each substance, and (b) this critical size is of the order of only a few "molecules" or ion pairs. These two conclusions are contradictory to those of TURNBULL. These two kinetic approaches to nucleation have been reviewed and summarized by KLEIN AND GORDON[13]. It should be emphasized that the TURNBULL approach is a theoretical one with the conclusions not based upon measurements on practical precipitation systems and that the CHRISTIANSEN AND NIELSEN conclusions are based upon laboratory measurements on precipitation reactions. KLEIN, GORDON AND WALNUT[14] reported results of a different type of experiment from which it was also concluded that the nucleus consists of several ions rather than tens or hundreds.

The possibility of induced nucleation, which is nucleation not resulting entirely from random aggregation of a cluster of ions of sufficient size to form a nucleus, has often been encountered in measurements of critical supersaturation. It was found that precipitation from a metastable state could be initiated not only by seed crystals of the substance but also by such varied factors as exposure to air (city air was found to be more effective than country air in one report of 1865 quoted in reference 3), by stirring (copper stirring rod much more effective than platinum and slightly more so than glass[15]), by mechanical shock and by impurities in the reagents[16-18].

The possibility of induced nucleation has also been considered in some of the more recent kinetic studies of nucleation, but generally as a substitute for the usual nucleation process and not as a conceivably necessary part of it. TURNBULL[6] has suggested that induced nucleation may have been involved in the CHRISTIANSEN-NIELSEN experiments[7] on timing the induction period. NIELSEN[18] reported, on the basis of some experiments on barium sulfate in which the containers were cleaned in live steam prior to use, that most and perhaps all of the crystals originated on the walls of the vessel and not from spontaneous nucleation; he did not specifically relate this conclusion to his earlier work on induction periods or to the metastable state. MANSON, CAGLE AND EYRING[19] discussed, in conjunction with a study of the nucleation of ice crystals from supercooled water vapor in the presence of silver iodide seeds, the interconnected roles of induced nucleation and self-nucleation.

Earlier reports from this laboratory have shown that the size and number of precipitated particles may be markedly influenced by the presence of "addition agents"[20] by the age of a solution prior to use[20-22], by the physical form of the reagents[22] and by the time of contact of a reagent solution with an inert electrolyte[22]. Additional experimental data are presented here to show the effect of the past history of the solvent used in preparing a reagent solution and of the nature of the container upon the size and number of precipitated particles.

EXPERIMENTAL METHODS AND DATA

All chemicals were of reagent grade or of comparable purity. Precipitates of barium sulfate were prepared by adding an approximately 0.02 M solution of barium chloride at 60° in slight excess to an approximately 0.015 M solution of potassium sulfate at 30° and at pH 1. These conditions were chosen empirically to yield precipitates of fairly reproducible physical form. Generally at least six precipitations were performed for each size determination. All six were observed in a light microscope to check uniformity, and particle sizes were measured on at least two of the six by means of an ocular micrometer on the microscope. Some precipitates included fragments which may have broken off of larger dendritic crystals. TAKIYAMA[23] has shown that each large dendrite is a single crystal arising from a single nucleus. Only the larger crystals within each batch were measured in order that the resultant data would clearly show trends in crystal size variation.

Results of a series of experiments using water of varied past histories in preparing the barium chloride solution are shown in Table I. The effect of the age of the barium chloride solution is evident, but this factor has been discussed elsewhere[20-22,24]. Of particular significance now is the fact that the history of the water prior to preparing the solution of one of the reactants exhibits a large effect upon the particle size of the precipitate and thereby upon the number of nuclei which form and persist throughout the precipitation reaction. It hardly seems possible that this factor could influence the extent of a purely spontaneous process of nucleation. It is much more likely that the nucleation is induced, and that the effective number of particles which are induced is fewest with the purest water (D), next fewest with the next purest water (C), and that standing in pyrex (B) removed via adsorption some of the centers for induced nucleation which were initially present in the least pure water (A).

TABLE I

EFFECT OF THE PAST HISTORY OF THE WATER IN THE BARIUM CHLORIDE SOLUTION UPON THE PARTICLE SIZE OF BARIUM SULFATE

Age of $BaCl_2$ solution (h)	*Particle sizes (μ)*			
	Water A	*Water B*	*Water C*	*Water D*
0.5	9	9	9	9
1	11	—	13	13
2	13	—	18	20
4	16	18	23	28
8	16	—	31	40
24	16	45	56	68
48	16	45	68	78

Water A: lab. distilled water. Water B: lab. distilled water after standing 24 h in pyrex prior to dissolving $BaCl_2$. Water C: freshly distilled in all-pyrex system. Water D: freshly prepared (Barnstead) conductivity water.

It was also found that preheating of water for a time, then cooling and dissolving the barium chloride, resulted in much larger particles of the eventual precipitate of barium sulfate than did the use of water that had not received the heat treatment. In Table II are listed data from a series of experiments on preheating the water in various types of containers. Again it appears that nucleation must be induced, not entirely

TABLE II

EFFECT OF TYPE OF CONTAINER DURING PREHEATING OF WATER IN THE BARIUM CHLORIDE SOLUTION UPON THE PARTICLE SIZE OF BARIUM SULFATE

Age of $BaCl_2$ solution (h)	*Particle sizes (μ)*			
	Control (no heating)	*Pyrex*[a]	*soft glass*[a]	*Platinum*[a]
1	11	11	11	11
30	13	42	23	18
85	16	42	28	23
180	18	25	41	28
230	18	18	33	37
330	16	13	23	23
400	13	13	16	13
980	13	9	13	13

[a] Water heated 24 h at 80° prior to dissolving $BaCl_2$.

spontaneous. Preheating the water used in preparing one of the reagent solutions alters the number and/or the effectiveness of the sites upon which nucleation can occur, and the nature of the surfaces of the container is of significance.

DISCUSSION

The data of Tables I and II show that the number of nuclei which form and persist as single crystals throughout a precipitation reaction is considerably influenced by the type of water used in preparing the solution of a reactant and that even the type of container in which that water has been allowed to stand prior to use is significant. These observations are entirely consistent with earlier published information that virtually all circumstances brought to bear upon a precipitation medium can influence the physical characteristics of the precipitate. It is highly doubtful that some of these factors could influence a purely spontaneous nucleation process in which a group of ions of the desired substance cluster together to form a crystal nucleus, but it is conceivable that all of the factors could influence an induced nucleation reaction.

Mechanism of nucleation of ionic precipitates

The following suggestion is now made concerning the mechanism of nucleation of ionic precipitates. Most and very possibly all solutions inevitably contain available sites upon which crystals of a precipitate may be initiated, and these sites cause most and perhaps all nucleation processes in practical analytical precipitation reactions to be induced. Some of these sites are more effective in fulfilling this function than others. The number of available sites and their distribution with respect to effectiveness vary widely with conditions. In order for a crystal to get started, the solution in contact with a solute must be critically supersaturated with respect to that site. Random or statistical fluctuations exist, of course. Each site has a characteristic necessary critical supersaturation value. For a given number and distribution of sites, the number of sites which are used is a direct (but not simple) function of the degree of supersaturation. During subsequent growth of a crystal, the initiating site may be completely entrained within a crystal or the site may become separated from it.

This suggested mechanism of nucleation retains many of the features of other concepts, but it differs in three ways: (a) in considering nucleation sites or induced nucleation to be virtually necessary in practical situations and not merely possible, (b) in considering the overall nucleus to be physically different from that portion of the nucleus containing the lattice ions, and (c) in considering the critical supersaturation value to be a definite one for each available site but to vary widely from one site to another within a single solution. The available sites serve, in effect, as nucleation catalysts in a manner analogous to that described by MANSON, CAGLE AND EYRING[19] for the nucleation of ice crystals on silver iodide seeds.

Origin and function of the available sites

The function of an available site is simply to accumulate ions from the surrounding solution. The mechanism of attraction could be predominantly electrical, although more specific forces of attraction doubtlessly would occur in some cases. Ions of a charge opposite to that on the site would be attracted to it, including some of the eventual lattice types of ions. This "primary adsorbed" group of ions would in turn attract ions of opposite charge and, insofar as the primary group consisted of one type of lattice ion, the "secondary" group would specifically be of the other type of lattice ion. This grouping of lattice ions including the original site upon which it was accumulated is the particle which replaces the nucleus in the sense in which TURNBULL used the term. This is the solid particle which, in subsequent growth, requires work to extend the interface between particle and solution but which is already much larger than the few lattice ions grouped on its surface. Further growth can occur only on one part of the surface of this larger nucleus, but crystal growth frequently occurs selectively at certain points, corners, etc., even on much larger crystals. The grouping of lattice ions on the available site, but not including the site, is the critical nucleus in the sense in which CHRISTIANSEN AND NIELSEN used the term.

The relative effectiveness of a site is determined by the attractiveness which it has for one or the other type of lattice ion. The ideally effective site would be on a crystal of the precipitate itself, on which nucleation as a process distinct from crystal growth is by-passed. Other sites which exhibit specific attraction for one of the desired lattice ions would also be quite effective, such as sites on crystals of another substance containing one ion in common with the desired precipitate or of similar crystalline morphology. However, any surface which exhibits an electrical charge in the environment of the solution could serve as a site of effectiveness sufficient for it to function within the high degrees of supersaturation which may be achieved in the precipitation of slightly soluble substances. The site must be sufficiently large in area to hold a "CHRISTIANSEN-nucleus" of several lattice ions, and the entire solid particle or surface including the available site must be large enough to serve as a "TURNBULL-nucleus".

The sources of available sites are widely varied. They include the surfaces of the container, colloidal contaminants brought in by the solvent, colloidal impurities brought in by the reactants or by some other components of the reactant solutions, residues present from incomplete dissolution of a reagent, and the air.

Nucleation may conceivably occur in a limiting case by a purely spontaneous clustering together of a sufficiently large number of ions of the desired precipitate. However, it is very doubtful that any practical medium of precipitation is sufficiently free of available sites to preclude the possibility of induced nucleation. Surfaces of containers are always in contact with reactant solutions. Some experiments have been conducted in which precipitation occurs within droplets of a spray, but even then the reactant solutions have been in contact with walls of containers prior to the precipitation.

No chemical reagent is of absolute purity, and even a trace of impurity could provide many available sites. For example, consider 0.1 g of a reagent used to form 0.1 g of a precipitate of density 2 and of cubic particles 1 μ on an edge. The precipitate would consist of $5 \cdot 10^{10}$ particles. This number of impurity sites, allowing a cube of the same density and 50 Å on an edge for each site, would weigh $1.25 \cdot 10^{-8}$ g or only about 0.1 p.p.m. of the 0.1 g of reagent. Soluble reagent chemicals meeting A.C.S. purity designations may typically contain up to 50 or 100 p.p.m. of "insoluble matter", far more than enough to provide the nucleation sites. Perhaps the entrainment of available sites during manufacture of the chemicals is a reason for the presence of this impurity within reagent grade-chemicals. In addition, a nucleating site may become separated from a growing crystal and serve to nucleate another crystal in the same reaction. It is interesting to note that even the sulfur, the boiling point of which has been used as one of the defining temperatures on the international temperature scale, has been found to contain sufficient impurity of heavy hydrocarbons to alter[25] the melting point by 0.7°.

Relationship to other factors

If the available sites do play a virtually necessary role in the nucleation of ionic precipitates, other valid experimental facts and principles must be consistent with this concept. Numerous experimentally determined facts have already been attributed to induced nucleation. Space here permits mentioning only a few which have not been specially related to induced nucleation of the type described in this paper.

The irreproducibility of experimental measurements of critical supersaturation values[2,3,5] could result from random fluctuations in conditions, such as past history of the solvent and the containers[18].

The discrepancies concerning whether there is a critical nucleus size or not and whether the nucleus contains several ions or from tens to hundreds of ions[6,7,13] could arise from referring to the two different entities as the nucleus. This suggestion is entirely consistent with the approaches used in the past in getting the contradictory conclusions.

Addition agents[20] can markedly influence the size and number of particles obtained by (a) providing new available sites and/or (b) competing for sites already available to make them less effective. In like manner ionic strength[17] could influence the number and distribution of available sites. The increase in number of particles caused by the presence of a detergent in the precipitation medium[26] could result from nucleation sites provided by micelles of the detergent or from trace impurities.

Use of a solid reagent which dissolves and immediately enters into precipitation reaction in comparison to use of solution reagents[22], not only modifies the extent of supersaturation but also provides many additional sites which would be expected to be of relatively high effectiveness. A freshly dissolved foreign electrolyte[22] results in a different number of particles than the same electrolyte not freshly dissolved because of the sites introduced by that electrolyte, some of which may become adsorbed on or combined with other sites upon standing. The interesting observation[27] that seed crystals which have been aged in a mother liquid are less effective in relieving critical supersaturation than "fresh" seed crystals could result from a coating during aging, perhaps by a hydrolysis product as suggested by the authors, of the surface sites to render them less effective.

The fact that, as the concentration of reactants is increased, the size of particles increase to a maximum and then decrease[4,28] could arise from the interrelated effects of extent of supersaturation attained and the increasing number of sites available at the higher degrees of supersaturation. The fact that, over narrower ranges of concentration, the number of particles is constant[11,29] could arise from equal numbers of sites available within the range of supersaturation reached.

In homogeneous precipitation processes, nucleation is generally not strictly one of homogeneous reaction[30], but it generally does occur under conditions of less supersaturation than in the usual direct mixing of reactants. So only the more effective sites are utilized. It is interesting to note that sulfide precipitates, whether formed directly by hydrogen sulfide or homogeneously by hydrolysis of thioacetamide, contain some sulfur, which could be involved in the induced nucleation. TURKEVICH[31] found a colloidal particle to be involved in the nucleation of colloidal gold.

The effects of stirring and mechanical shock in relieving supersaturation[2,3,15] may result not only from additional sites made available but also from breaking off sites already in use to serve again.

The effects noted in comparing precipitates obtained from fresh and aged solutions of a reactant[20,21,24] could result from introduction of available sites with the dissolving reagent, their subsequent removal by adsorption on the walls of the container or by dissolving or by combination with one another, followed eventually by introduction of still more sites from exposure to the air.

The fact that a solution in an extremely slow homogeneous precipitation process can increase in concentration beyond that at which precipitation begins and can remain thus for many minutes[32] could arise from the use of the most effective sites at the lower concentrations and then some sites of less effectiveness at higher supersaturations.

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SUMMARY

Data have been presented which show that the particle size of a precipitate is influenced by the past history of the water used in preparing a reagent solution. On the basis of these data and previously published information it is proposed that the nucleation process in practical analytical precipitation reactions is one of induced nucleation on sites which are inevitably available. It has been shown that such a mechanism is free of inconsistencies encountered with other proposals concerning the origin of nuclei.

RÉSUMÉ

Il est démontré que la pureté de l'eau utilisée pour la préparation des réactifs a une grande influence sur le nombre de germes de cristallisation et sur la grosseur des grains du précipité formé.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass die Reinheit des zur Herstellung der Reagenzienlösungen verwendeten Wassers einen grossen Einfluss auf die Zahl der Kristallkeime und Korngrösse des gebildeten Niederschlages ausübt.

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EFFECT OF FORM OF REAGENT ON PARTICLE SIZES OF PRECIPITATES

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The usual method of forming a precipitate in an analytical procedure is to mix solutions of the appropriate reagents. The particle size of the precipitate is influenced by numerous experimental conditions, including in some cases the age of one of the solutions at the time of its use[1–3]. For example, when a solution of freshly dissolved barium chloride is used for the precipitation of barium sulfate, the particles of the precipitate are much smaller than are those formed when the barium chloride solution is allowed to stand at room temperature for several hours prior to use. In research upon this phenomenon it is not possible to use a reagent solution of absolute freshness. However, it is possible to form a precipitate by introducing one reactant as a solid into a solution of the other reactant, so the solid reagent enters in the precipitation as rapidly as it dissolves. The situation is similar to, but obviously not identical with, that of a reagent solution of zero age.

The purposes of the present investigation are (a) to form several precipitates both by use of two solutions and by use of a dissolving solid as one of the reactants and to compare the particle sizes of the resultant precipitates, (b) to observe the relationship of this factor to other conditions of precipitation and (c) to interpret the results with reference to mechanisms of nucleation and crystal growth.

EXPERIMENTAL METHODS

All chemicals were of reagent grade or of comparable chemical purity and were used without further purification. The water used in preparing all solutions was first distilled and then deionized and kept in a polyethylene storage container until used.

Particle sizes were determined directly by microscopic methods employing the light microscope for particles about one micron and larger in average dimension and the electron microscope for particles about five microns and smaller. Both microscopic methods yielded similar results when used on the same precipitate.

In some of the experiments particle sizes of equal mass-concentration suspensions were compared by measuring their optical densities in a Bausch and Lomb Spectronic 20 Colorimeter. The relationship between particle size and light scattering is very complex. But the optical density can be taken as an inverse measure of relative particle size, at least for particles which are appreciably larger than the wavelength of light. This relationship is justified empirically by the data of Table I, in which are listed the optical densities and the size data obtained with a microscope for a series of barium sulfate suspensions. A plot of these data in terms of optical density *vs.* 1/size is a straight line.

TABLE I

DIRECT COMPARISON OF OPTICAL DENSITY OF SUSPENSION WITH PARTICLE SIZE OF PRECIPITATE

Optical density	*Average particle size (μ)*
0.37	17.4
0.42	14.9
0.45	14.1
0.45	13.9
0.47	15.5
0.48	12.2
0.56	10.1
1.08	4.8

The microscopic methods of size determination are advantageous in that they provide actual size numbers and also permit observation of morphology and size distribution if desired. The optical density method of size comparison is advantageous in that it is much quicker and is free from the possible error of segregation of large and small particles during mounting for microscopic observation.

EXPERIMENTAL DATA

Lead sulfate, barium chromate and calcium sulfate were precipitated, first with two reagent solutions and then with one solid reagent plus one solution reagent. When a solid reagent was used, it was in excess so slight variation in weight from one trial to another would not influence the mass of precipitate formed. The volumes and concentrations were such that the molar concentration of precipitate, assuming it to be suspended uniformly, would be constant in all precipitations of each of the three substances. Optical density measurements were made and considered to be inversely related to average particle size. Results of both optical density and microscopic observations of the precipitates are tabulated in Table II. It was also found that addition of two solids, lead nitrate and sodium sulfate, to water resulted in still smaller crystals of lead sulfate, about 1.5 μ in average dimension.

The data of Table II reveal that (a) the crystal sizes of precipitated lead sulfate and calcium sulfate are not significantly influenced by which reagent is in excess and (b) the use of a solid reagent causes a much smaller particle size than does use of two

TABLE II

MEASUREMENTS OF PARTICLES FORMED BY SOLID REAGENT AND BY SOLUTION REAGENTS

Precipitate	*Reagents*	*Optical density*		*Appearance in microscope*
		*Mean**	*S. D. of mean*	
$PbSO_4$	2 ml 0.10 M $Pb(NO_3)_2$ 2 ml 0.05 M Na_2SO_4	0.61	0.02	rectangular, 30 × 3 μ
$PbSO_4$	2 ml 0.05 M $Pb(NO_3)_2$ 2 ml 0.10 M Na_2SO_4	0.63	0.01	rectangular, 30 × 4.5 μ
$PbSO_4$	0.05 g $Pb(NO_3)_2$ 4 ml 0.025 M Na_2SO_4	0.82	0.03	rectangular, 9 × 3 μ
$PbSO_4$	4 ml 0.025 M $Pb(NO_3)_2$ 0.03 g Na_2SO_4	0.87	0.04	rectangular, 18 × 4.5 μ
$BaCrO_4$	2 ml 0.10 M $BaCl_2$ 2 ml 0.05 M Na_2CrO_4	1.83	0.02	** 1.5 μ
$BaCrO_4$	0.05 g $BaCl_2$ 4 ml 0.025 M Na_2CrO_4	1.70	0.02	** 1.5–3 μ
$CaSO_4$	2 ml 2.0 M $Ca(NO_3)_2$ 2 ml 1.0 M Na_2SO_4	0.33	0.02	rectangular, 9 × 3 μ
$CaSO_4$	2 ml 1.0 M $Ca(NO_3)_2$ 2 ml 2.0 M Na_2SO_4	0.33	0.01	irregular, 6 μ
$CaSO_4$	0.90 g $Ca(NO_3)_2 \cdot 4\ H_2O$ 4 ml 0.5 M Na_2SO_4	0.35	0.01	rectangular, 4.5 × 1.5 μ
$CaSO_4$	4 ml 0.5 M $Ca(NO_3)_2$ 0.60 g Na_2SO_4	0.36	0.01	irregular, 3 μ

* Each mean represents at least 5 replicate precipitations, generally 10.
** Apparently spheres, but not clearly resolved.

reagent solutions for lead sulfate and slightly so for calcium sulfate but not for barium chromate.

Several experimental variables were studied in the precipitation of lead sulfate. The following reference conditions were arbitrarily selected: room temperature; solid lead nitrate with particle size of 120–150 μ; solid sodium sulfate with particle size of 60–90 μ; sulfate ion in stoichiometric excess; both solid reagents added with hand swirling to deionized water at neutral pH. Variations from these reference conditions were found to exhibit the effects listed in Table III. It is evident that the smaller size

TABLE III

EFFECTS OF SEVERAL VARIABLES ON PARTICLE SIZE OF LEAD SULFATE PRECIPITATED BY SOLID REAGENTS

Variable	*Effect*
higher temperature	slightly smaller crystals
larger particle size of reagents	much larger crystals
smaller particle size of reagents	much smaller crystals
no stirring	no difference
vigorous stirring	same size, but crystals more perfect
stirring by bubbling air	same size, but crystals more perfect
change in volume of water	no difference
1 : 1 ethanol–water medium	slightly smaller crystals
low pH	no difference
other reagent in excess	no difference

resulting from use of solid reagents is very real and is not dependent upon some chance interaction of other conditions. Apart from the use of larger particles of the solid reagents, none of these variations in conditions removed or even decreased the effect of the use of the solid reagents.

Effect of particle size of the solid reagent

Additional experiments were performed on barium, calcium and lead sulfates to obtain further information on the effect of the particle size of a solid reagent upon the particle size of the precipitate. A barium sulfate precipitated by mixing solutions of barium nitrate and sodium sulfate consisted of dendritic crystals with overall sizes of about 22–30 μ. When one large crystal of barium nitrate was added directly to the sulfate solution, the crystals of precipitated barium sulfate were still somewhat dendritic but were only about 12 μ. When the barium nitrate was added as a finely divided substance, the precipitated particles were of similar morphology but only about 1.5 μ.

Calcium sulfate was precipitated, both with large crystals of calcium nitrate and with finely divided crystals, each added to a sulfate solution. The crystals precipitated by the latter were only one-third as large as the former, although there was much variation of size within each.

Barium and lead sulfates were precipitated with solid sodium sulfate of several different particle sizes. The most finely divided sodium sulfate which could be obtained by hand-grinding was about 6 μ. To obtain even smaller particles for this experiment, a solution of sodium sulfate was passed through an atomizer ("Vaponefrin Nebulizer") operated continuously by compressed air, and the tiny droplets were evaporated by heat and their residues collected. The intention was to force evaporation of each tiny droplet of the solution to leave one or more tiny crystals of sodium sulfate as the residue from each droplet. No difficulty was experienced in evaporating the droplets readily, but the efficiency of collecting the tiny crystals from the air was never over 20% in the several methods tried. The particles of sodium sulfate which were thus obtained ranged down to one-tenth μ as determined by examination in the electron microscope. These particles were used as solid reagents in the precipitation of barium and lead sulfates, and the resulting precipitates consisted of smaller crystals than those obtained either by use of larger particles of solid reagent or of solution reagents.

It is concluded that the use of a solid reagent in place of one of the solution reagents results in a precipitate of smaller crystals and that the effect is enhanced as the particle size of the solid reagent is decreased.

Some other precipitates

Six other precipitates were formed, both by means of two solutions and by means of one solid reagent plus one solution reagent in order to establish further how general the effects are. All precipitates in this series were observed in the electron microscope. In five of them, calcium fluoride, lead fluoride, nickel dimethylglyoxime, strontium sulfate and silver chromate, it was found (a) that the use of a solid reagent results in particles from one-third to one-tenth of the size obtained when both reagents were used as solutions and (b) that the effect is enhanced by finely grinding the solid reagent prior to use. Therefore these two conclusions appear to be very definite and quite general. Data on the sixth precipitate, silver chloride, were inconclusive, although this precipitate probably fits into the general pattern as well.

Effect of the presence of a freshly dissolved inert electrolyte

As an aid in interpreting the results of the preceding experiments in terms of nucleation and crystal growth, a series of experiments was conducted to determine whether or not the presence of a recently dissolved inert electrolyte (one which is not a direct reactant in the precipitation process) would exert any influence on the particle size of the precipitate. Four precipitates were selected for study, strontium sulfate, lead fluoride, lead chromate and barium sulfate. Two inert electrolytes, sodium nitrate and potassium nitrate, were each used with each of the four precipitates. The major reactants were used as solutions throughout. All precipitations were run at least in triplicate, and optical density measurements were made for comparison of particle sizes. In all four precipitation reactions and with each of the two inert electrolytes, the presence of a recently (0.5 to 1.0 min) dissolved inert electrolyte influenced the particle size, and in every case the influence was different in magnitude and/or in direction to the effect of the same inert electrolyte which had been in solution for a longer period of time. It is concluded (a) that the presence of a freshly dissolved inert electrolyte at the time that a precipitation process occurs very markedly influences the particle size of the precipitate and (b) that this influence can not be attributed solely to the presence of the ions of that inert electrolyte.

DISCUSSION

The fact that use of a solid reagent results in smaller particles of a precipitate than does use of solution reagents signifies that the solid reagent somehow enhances nucleation at the expense of crystal growth. It is now of interest to consider possible reasons for this enhanced nucleation.

According to classical Von Weimarn concepts, the rate of nucleation and thereby the number of particles is a function of the degree of supersaturation at the time the particles form. If this be the determinative factor in the present situation, the degree of supersaturation would be greater when a solid reagent is used than when all reagents are in the form of solutions. However, such may not be the case. Considering first the overall bulk of the precipitation medium, the supersaturation must be less with a solid reagent, because the reagent ions are used up in forming the precipitate as rapidly (or nearly so) as they enter the solution from dissolution of the solid reagent.

Considering second not the overall bulk of the precipitation medium but only the immediate environment as the added reagent meets the other reagent (where the drops "hit" in using solutions and the surfaces of the dissolving particles in using a solid), it is more difficult to compare the extents of supersaturation in the two cases. Three factors conceivably could influence the temporary, localized degrees of supersaturation. (Let X represent the solid reagent and Y the solution of the same reagent, each added to a solution of the other requisite reagent.) (a) X is more concentrated than Y, tending to make greater supersaturation with X than with Y. (b) Y is added all quite abruptly by pouring in, whether dropwise or not, while X is effectively added only at its dissolution rate, tending to make greater supersaturation with Y than with X. (c) The area of contact with X is the surface area of the particles which, except when only a few large crystals are used, is greater than the area of contact where two liquids hit each other; thus the area (and volume) of supersaturation is spread out more in *X* than in *Y*, tending to make greater supersaturation with *Y*. These factors are interrelated, especially (a) and (b). If factor (a) were predominant, the rate of stirring would be expected to influence the number of nuclei formed, but the data of Table III indicate that this is not the case. From these considerations it may be tentatively concluded, but is not proved, that even the localized extent of supersaturation with a solid reagent is no greater than that with solution reagents. If this be true, the larger number of crystals resulting from use of a solid reagent can not be accounted for by a consideration of the relative degrees of supersaturation in the two cases.

Of more direct significance in this connection are the results of the experiments with inert electrolytes. The extent to which a solution is supersaturated with respect to barium sulfate, for example, can not be influenced by whether some sodium nitrate also present has been there for one minute or for an hour.

The presence of the solid phase must directly enhance nucleation, possibly by providing additional surfaces upon which nucleation can get started. This mechanism is discussed in a broader context in another paper from this laboratory[4].

CONCLUSIONS

1. A precipitate formed by mixing one solid reagent with one solution reagent consists of particles which are much smaller than are those formed when solutions of the two reagents are mixed. The phenomenon occurs in the precipitation of lead sulfate, calcium sulfate, barium sulfate, strontium sulfate, calcium fluoride, lead fluoride, nickel dimethylglyoxime and silver chromate, so it is quite general.
2. The effect is enhanced as the particle size of the solid reagent is decreased.
3. The presence of a freshly dissolved inert electrolyte at the time two solutions are mixed to form a precipitate influences the particle size of a precipitate, and this effect can not be attributed solely to the presence of the ions of that inert electrolyte.
4. The effects can probably not be attributed to the degrees of supersaturation existing at the time that the precipitate is formed.
5. The presence of the solid phase must directly enhance nucleation. Combining these results with those reported earlier on the aging of solutions, it appears that the presence or the recent presence of a solid phase, whether of one of the main reactants or not, enhances nucleation by providing sites upon which the formation of nuclei may be induced.

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SUMMARY

The particle size of an ionic precipitate is much smaller when one of the reactants is introduced as a solid rather than as a solution. The effect is enhanced as the particle size of the solid reagent is decreased. The presence of a freshly dissolved inert electrolyte also influences the particle size of a precipitate. The affects are not attributable merely to the degree of supersaturation but rather to the provision by the freshly dissolved material of sites upon which nucleation can be induced.

RÉSUMÉ

L'auteur a étudié l'effet, sur la grosseur des particules d'un précipité, de la forme sous laquelle le réactif est utilisé (à l'état solide, ou en solution). Il a examiné également l'influence d'un électrolyte neutre.

ZUSAMMENFASSUNG

Der Einfluss der Form (fest oder gelöst) eines Fällungsmittels auf die Korngrösse eines gebildeten Niederschlages wurde untersucht. Zugabe eines neutralen Salzes kurz vor der Fällung beeinflusst ebenfalls die Korngrösse des Niederschlages.

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DETERMINATION OF NIOBIUM AND TANTALUM WITH CINNAMYL HYDROXAMIC ACID AND N-CINNAMOYL-N-PHENYLHYDROXYLAMINE

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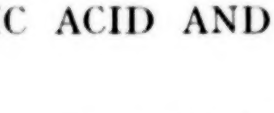
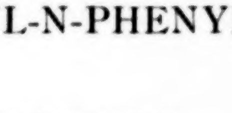
We have shown that N-benzoyl-N-phenylhydroxylamine[1] is a suitable reagent for the separation of niobium and tantalum, and for the direct gravimetric determination of niobium[2]. Further investigations have been carried out to discover if other reagents with similar atomic groupings could be equally useful. Organic derivatives of hydroxamic acids are structurally related to N-benzoyl-N-phenylhydroxylamine and may be regarded as derived from hydroxylamine, NH_2OH, by the replacement of one or both of the hydrogen atoms linked to nitrogen.



$$\begin{array}{l} C_6H_5 - C = O \\ \qquad\quad | \\ C_6H_5 - N - OH \end{array}$$

N-benzoyl-N-phenylhydroxylamine



$$\begin{array}{l} C_6H_5 - C = O \\ \qquad\quad | \\ H - N - OH \end{array}$$

Benzohydroxamic acid

Of the organic hydroxamic acids prepared, benzohydroxamic acid and phenylacetylhydroxamic acid formed no precipitate with niobium or tantalum in tartrate solution, even when it was made ammoniacal. Salicylhydroxamic acid formed insoluble complexes with both niobium and tantalum, but the reaction was not strictly quantitative when the solution contained oxalate, tartrate or citrate. Cinnamylhydroxamic acid, however, quantitatively precipitated both niobium and tantalum under different pH conditions. When oxalate or tartrate was present, both niobium and tantalum could be precipitated from solutions of acidity anywhere between 5% by volume of sulphuric acid and a maximum pH of 6.5; with citrate, precipitation was satisfactory up to pH 2.0 for tantalum and 2.8 for niobium. At acidities above 5% of sulphuric acid or at pH above 6.5 the complexes became more soluble. Though cinnamylhydroxamic acid failed to give a clean separation of niobium and tantalum from each other, these metals could be separated from other elements in presence of EDTA, and niobium could be determined by direct weighing of the stable complex $NbO\,(C_9H_8NO_2)_3$, which decomposed only at 225°. The tantalum precipitate, however, had to be ignited to the pentoxide before the final weighing.

Of the derivatives of phenylhydroxylamines, N-phenylacetyl-N-phenylhydroxylamine gave only incomplete precipitation of niobium and tantalum on prolonged digestion with oxalate or tartrate solutions.

N-cinnamoyl-N-phenylhydroxylamine, however, behaved like N-benzoyl-N-phenylhydroxylamine and precipitated niobium under the same conditions. With the N-cinnamoyl reagent the pH range for complete precipitation extended up to a maximum of 7.5. The niobium complex was not very stable to EDTA and had to be ignited to the oxide because it was always associated with the sparingly soluble reagent. With tantalum, N-cinnamoyl-N-phenylhydroxylamine required an oxalate or tartrate medium containing 2.5 to 10% by volume of sulphuric acid; with less acid the tantalum complex was colloidal.

Although N-cinnamoyl-N-phenylhydroxylamine does not permit the separation, by a simple pH adjustment, of the earth acid elements from each other, it allows the separation of niobium and tantalum from a large number of ions, *e.g.* Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, Mg^{+2}, Be^{+2}, Cu^{+2}, Hg^{+2}, Cd^{+2}, As^{+3}, Bi^{+3}, Al^{+3}, Cr^{+3}, UO_2^{+2}, Th^{+4}, Ce^{+4}, PO_4^{-3} and AsO_4^{-3}.

Details of the investigation of cinnamylhydroxamic acid and N-cinnamoyl-N-phenylhydroxylamine as reagents for the precipitation and separation of niobium and tantalum from each other and from other elements are given below.

EXPERIMENTAL

The chemicals and standard solutions used were the same as reported earlier[1,2]. Standard oxalate, citrate and tartrate solutions of niobium and tantalum were prepared[1-3] from specpure (Johnson and Matthey) Nb_2O_5 and Ta_2O_5. A Cambridge pH indicator was used for all pH measurements.

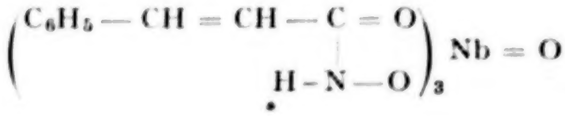
Cinnamylhydroxamic acid (m.p. 110–111°) was prepared according to the method of THIELE AND PICKARD[4]; a 1% freshly prepared aqueous solution was used as the precipitant.

A 2.5% alcoholic solution of N-cinnamoyl-N-phenylhydroxylamine, prepared according to the following procedure, was also used as a precipitant. To a cold solution of phenylhydroxylamine (30 g) in water (1200 ml) was added dropwise over a period of 90 min, a solution of cinnamoyl chloride (53 g) in ether (75 ml). The mixture was stirred vigorously by a mechanical stirrer and kept faintly alkaline throughout by occasional additions of sodium bicarbonate. Stirring was continued for a further 45 min. The mono-derivative was then separated and recrystallised from alcohol in the same way as for N-benzoyl-N-phenylhydroxylamine. The pale green crystals melted at 158–160°. Analysis showed that the formulae of the N-phenylacetyl-N-phenylhydroxylamine and N-cinnamoyl-N-phenylhydroxylamine were, respectively, $C_{14}H_{13}NO_2$ (% calc.: C, 73.99; H, 5.77; N, 6.16; % found: C, 74.01, 74.03; H, 5.78, 5.77; N, 6.14, 6.12), and $C_{15}H_{13}NO_2$ (% calc.: C, 75.29; H, 5.48; N, 5.85; % found: C, 75.20, 75.36; H, 5.43, 5.46; N, 5.81, 5.82).

Composition of cinnamylhydroxamic acid complex

The yellow niobium and the white tantalum complexes were isolated by the procedure given below for their estimation and dried at 110°. The percentage of the element in the respective complexes was determined by igniting a known amount of the dried complex and weighing as the pentoxide. The nitrogen contents were determined by Kjeldahl's method. The niobium complex was found to have the composition $NbO(C_9H_8NO_2)_3$ (% Nb calc.: 15.60; %N calc.: 7.09; %Nb found: 15.27, 15.56; % N found: 7.02, 7.05).

Structurally the complex may be represented as follows:



$$\left(\begin{array}{r} C_6H_5-CH=CH-C=O \\ | \quad \\ H-N-O \end{array}\right)_3 Nb=O$$

The thermolysis curve (Fig. 1) showed that the niobium complex could be easily dried at 110°; it is stable up to 225° and at higher temperatures decomposes slowly to pentoxide; thermolysis of the tantalum complex proved the absence of any definite composition. The niobium complex can therefore be directly weighed as $NbO(C_9H_8NO_2)_3$, but the tantalum complex must be ignited to the weighable pentoxide.

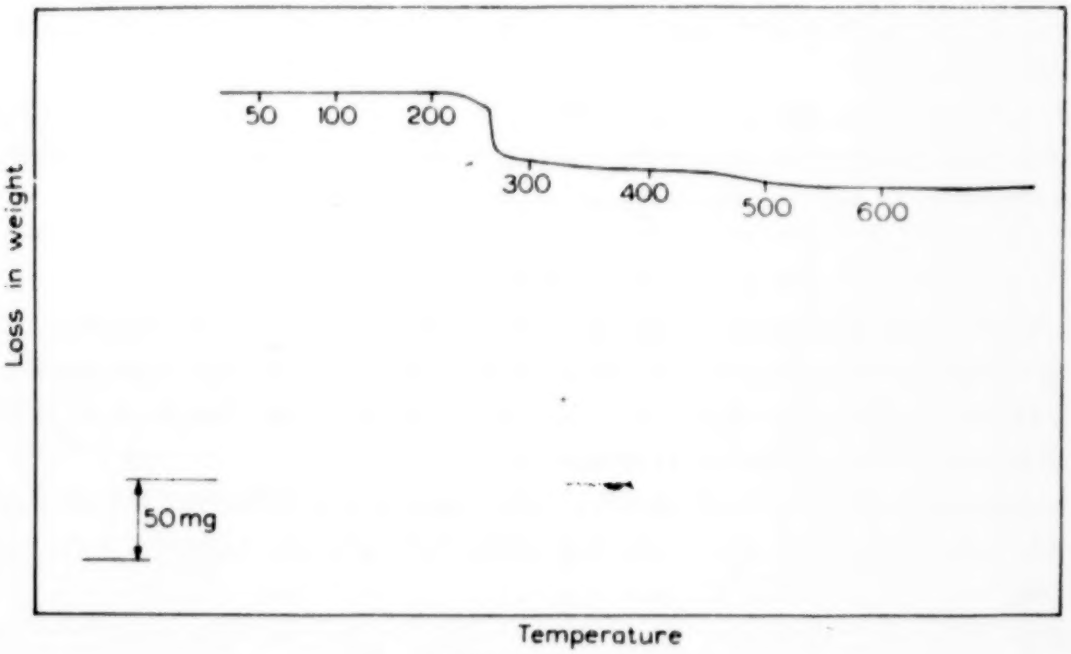


Fig. 1. Thermolysis curve.

Effect of pH and the determination of niobium and tantalum

(*a*) *With cinnamylhydroxamic acid*

An aliquot of the standard solution of niobium or tantalum was diluted to about 150 ml and the pH was adjusted with dilute sulphuric acid, ammonium acetate or ammonia. The solution was heated nearly to boiling, and an aqueous solution of the reagent was added with stirring till a slight turbidity appeared (25 ml of 1% solution was sufficient for every 10 mg of the pentoxide). The beaker was then placed on a boiling water bath for 30 to 60 min for the complete coagulation of the precipitate. The solution was then cooled to room temperature (30°) and the precipitate was filtered through a sintered glass No. 4 crucible, washed thoroughly with warm water (40°), dried at 110° and weighed. The weight of the complex multiplied by 0.2231 gave the weight of Nb_2O_5.

For tantalum, a few ml of a suspension of ashless paper pulp was added before the coagulation of the precipitate; after filtration through a quantitative filter paper the precipitate was washed with warm water containing 1% ammonium nitrate and 0.2% reagent. The precipitate was then dried, ignited and weighed as Ta_2O_5.

In presence of oxalate and tartrate, niobium and tantalum were quantitatively precipitated from solutions containing 5% (v/v) sulphuric acid or up to a pH of 6.5. For complete precipitation in presence of citrate, the acidity could be as high as 5% sulphuric acid but the pH had to be less than 2.0 for tantalum or 2.8 for niobium. Higher acidities or higher pH gave low results owing to incomplete precipitation (Table I).

TABLE I

pH	*Nb_2O_5 taken mg*	*Wt. of complex mg*	*Nb_2O_5 found mg*	*pH*	*mg Ta_2O_5*	
					taken	*found*
*[a]	15.0	48.7	10.86	*[a]	13.8	9.4
**[a]	15.0	66.3	14.80	**[a]	13.8	13.8
1.5[a]	15.0	66.8	14.9	1.3[a]	13.8	13.7
4.0[a]	15.0	67.0	15.0	4.2[a]	13.8	13.6
5.4[a]	15.0	67.0	15.0	6.4[a]	13.8	13.8
6.5[a]	15.0	66.5	14.8	8.6[a]	13.8	8.2
7.3[a]	15.0	56.2	12.54	0.8[b]	13.8	13.7
1.2[b]	15.0	66.3	14.80	2.0[b]	13.8	13.8
2.8[b]	15.0	66.5	14.80	2.6[b]	13.8	12.7
3.2[b]	15.0	64.0	14.30			

* 10% (v/v) H_2SO_4
** 5% (v/v) H_2SO_4
[a] oxalate or tartrate solution
[b] citrate solution

(*b*) *With N-cinnamoyl-N-phenylhydroxylamine*

An aliquot of the standard oxalate or tartrate solution of niobium or tantalum was diluted to about 250 ml, and dilute sulphuric acid or ammonia was added to adjust the pH to the desired value. The solution was heated nearly to boiling and niobium or tantalum was precipitated by following the procedure given under (*a*) (7.5 ml of 2.5% reagent solution was sufficient for every 10 mg of the pentoxide). The precipitate was finally ignited and weighed as the pentoxide. When the pH of the solution was less than 2.0, precipitation was done at room temperature (25–30°) to prevent the formation of a gummy precipitate.

The precipitation of niobium was quantitative from 10% (v/v) sulphuric acid solutions and from solutions of pH up to 7.5; for tantalum the acidity should be between 2.5 and 10% (v/v) sulphuric acid. At lower acidity the tantalum precipitate is colloidal. The results are given in Table II.

TABLE II

mg Nb_2O_5		*pH*	*mg Ta_2O_5*		*pH*
taken	*found*		*taken*	*found*	
18.3	18.3	*	13.4	13.4	*
18.3	18.3	**	13.4	13.3	**
18.3	18.3	0.5	13.4	13.3	***
18.3	18.2	3.2	13.4	11.0	0.6
18.3	18.2	5.1			
18.3	18.2	6.9			
18.3	18.3	7.5			
18.3	16.0	8.0			

* 10% (v/v) H_2SO_4
** 5% (v/v) H_2SO_4
*** 2.5% (v/v) H_2SO_4

Effect of various ions

(*a*) *With cinnamylhydroxamic acid*

Preliminary experiments showed that in presence of EDTA neither niobium nor tantalum was precipitated below pH 5.0. An aliquot of the standard oxalate or tartrate solution of niobium or tantalum was therefore mixed with a few ml of the solution of the ion whose effect was to be studied; the solution was diluted to 200 ml, and treated with sufficient EDTA to mask the ions, and the pH was adjusted by ammonium acetate to above 5.0. The niobium or tantalum was then precipitated, washed and weighed as described above. The results are given in Table III.

TABLE III

Ion	*Added mg*	*mg Nb_2O_5*		*mg Ta_2O_5*	
		taken	*found*	*taken*	*found*
Fe^{+3}	100.0	12.3	12.1	10.6	10.6
Al^{+3}	100.0	12.3	12.0	10.6	10.5
Cr^{+3}	100.0	12.3	12.3	10.6	10.8
Zn^{+2} Mn^{+2} Ni^{+2} Co^{+2}	100.0	12.3	12.4	10.6	10.4
Be^{+2} Mg^{+2}	100.0	12.3	12.4	10.6	10.6
Th^{+4}	120.0	12.3	12.5	10.6	10.6
UO_2^{+2}	120.0	12.3	12.2	10.6	10.7
Ce^{+4}	100.0	12.3	12.1	10.6	10.3
Cu^{+2}	100.0	14.6	14.5	15.0	15.2
Cd^{+2}	100.0				
Bi^{+3}	100.0				
Hg^{+2}	100.0				
As^{+3}	100.0	14.6	14.2	15.0	14.7
Sb^{+3}	100.0				
Sn^{+2}	100.0				
AsO_4^{-3}	100.0	14.6	14.7	15.0	15.0
WO_4^{-2}	100.0				
PO_4^{-3}	100.0				

(*b*) *With N-cinnamoyl-N-phenylhydroxylamine*

The effect of various ions was studied by the method described above with 10% (v/v) sulphuric acid. The results (Table IV) show that only Ti^{+4}, Zr^{+4}, VO_3^- MoO_4^{-2}, WO_4^{-2}, Fe^{+3}, Sn^{+2} and Sb^{+3} interfere.

TABLE IV

Ions	*Added mg*	*mg* Nb_2O_5		*mg* Ta_2O_5	
		taken	*found*	*taken*	*found*
UO_2^{+2}	200.0	16.0	16.0	11.0	11.1
Be^{+2}	100.0	16.0	16.1	11.0	11.1
Mg^{+2}	100.0				
Cu^{+2}	100.0	16.0	16.2	12.4	12.5
Cd^{+2}	100.0				
Hg^{+2}	100.0				
Zn^{+2}	100.0	15.2	15.2	12.4	12.4
Mn^{+2}	100.0				
Ni^{+2}	100.0				
Co^{+2}	100.0				
Al^{+3}	100.0	16.0	16.1	11.0	11.1
Cr^{+3}	100.0				
Bi^{+3}	100.0	15.0	15.1	12.4	12.5
As^{+3}	100.0				
Th^{+4}	250.0	16.0	16.0	11.0	11.0
Ce^{+4}	200.0	16.0	16.2	11.0	11.2
PO_4^{-3}	250.0	15.2	15.2	12.4	12.5
AsO_4^{-3}	240.0	15.2	15.3	12.4	12.6

SUMMARY

The determination and separation (from other ions) of niobium and tantalum by means of cinnamylhydroxamic acid and N-cinnamoyl-N-phenylhydroxylamine are described. Cinnamylhydroxamic acid permits the separation of both elements above pH 5.0 (titanium, zirconium and molybdenum interfere) and the niobium complex can be weighed after drying at 110°. With N-cinnamoyl-N-phenylhydroxylamine, the optimum conditions are slightly different; titanium, zirconium, vanadate, molybdate, tungstate, iron, tin and antimony contaminate these precipitates.

RÉSUMÉ

Une méthode est proposée pour le dosage du niobium et du tantale, et leur séparation d'avec d'autres ions. On utilise comme réactifs l'acide cinnamylhydroxamique et la N-cinnamoyl-N-phénylhydroxylamine.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Abtrennung und Bestimmung von Niob und Tantal mit Hilfe der Cinnamylhydroxamsäure und des N-cinnamoyl-N-phenylhydroxylamins.

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DOSAGE COMPLEXOMÉTRIQUE DE BROMURES ET D'IODURES EN PRÉSENCE L'UN DE L'AUTRE

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La méthode que nous décrivons est basée sur celle de BEKK[1], selon laquelle les deux halogènes sont précipités simultanément par addition d'un excès de nitrate d'argent. Ce précipité servira pour le dosage complexométrique.

On répète la même opération et le précipité de bromure et d'iodure d'argent est traité à chaud par un oxydant (mélange chromique). L'iodure est transformé en iodate alors que le bromure est décomposé en brome et libéré sous forme gazeuse. L'iodate d'argent est ensuite réduit en iodure au moyen d'une solution de sulfite de sodium. L'iodure d'argent est filtré, lavé et sert au dosage complexométrique.

La différence des lectures des deux titrages avec le complexon, permet de calculer les quantités de bromures et d'iodures présents. Les halogénures d'argent sont dissous dans une solution ammoniacale de tétracyanure de nickel suivant la technique de FLASCHKA ET HUDITZ[2,3]. Les réactions se passent comme suit:

$$2AgX + [Ni(CN)_4]^{-2} \rightarrow 2[Ag(CN)_2]^- + Ni^{+2} + 2X^-$$

Le nickel déplacé est dosé par voie complexométrique et l'halogène est ainsi déterminé indirectement.

Réactifs

Solutions de nitrate d'argent à 5% et à 0.1%; solution d'acide nitrique à 1%; solution de complexon III 0.1 *M*; solution saturée de murexide (aqueuse); solution ammoniacale de tétracyanure de nickel 0.1 *M*, obtenue par titrage précis d'une solution de sulfate de nickel 0.1 *M* avec une solution de KCN 1 *M* après addition d'ammoniaque, le titrage est terminé lorsque l'indicateur (murexide).vire du jaune au violet; bichromate de potassium (pro analisi); acide sulfurique concentré (pro analisi), solution concentrée de sulfite de sodium.

Mode opératoire

Les bromures et les iodures en solution sont précipités par la méthode usuelle en utilisant une solution de nitrate d'argent à 5%. Le précipité est filtré sur laine de verre et lavé deux fois avec une solution de nitrate d'argent à 0.1%, puis deux ou trois fois avec de l'acide nitrique à 1%. On répète la précipitation pour le dosage des iodures seuls.

Le premier précipité est conservé pour le dosage complexométrique des bromures et des iodures. Le second est traité (laine de verre et précipité) dans un bécher par une solution de 4 g de bichromate de potassium dans 60 ml d'acide sulfurique concentré, à 95°, et laissé sur le bain-marie pendant une demi-heure. Les iodures sont transformés en iodates alors que les bromures sont décomposés et le brome mis en liberté. Après digestion au bain-marie, on fait passer un courant d'air dans la solution pour chasser tout le brome.

Le contenu du bécher est dilué à 400 ml environ. On filtre et on lave bien le filtre avec de l'eau. On ajoute au filtrat, goutte à goutte, une solution concentrée de sulfite de sodium, en agitant constamment, jusqu'à ce qu'une faible odeur d'anhydride sulfureux persiste après un repos de 10 min. L'iodure d'argent se forme et précipite. On recueille le précipité d'iodure d'argent sur la laine de verre et on lave deux fois avec la solution de nitrate d'argent à 0.1%, puis deux à trois fois avec celle de l'acide nitrique à 1%.

Le précipité d'iodure d'argent est transféré (avec la laine de verre) dans un bécher contenant la solution ammoniacale de tétracyanure de nickel. On chauffe doucement en agitant le contenu du bécher jusqu'à dissolution complète du précipité. On ajoute quelques gouttes d'indicateur et l'on titre le nickel libéré avec la solution de complexon jusqu'à ce que la solution vire au violet. On note le nombre de ml de complexon utilisés.

Le précipité de AgI + AgBr est traité de la même façon et la lecture de la burette notée. On mesure la différence des deux lectures pour connaître la quantité de complexon nécessaire pour le dosage du brome. Les teneurs en mg d'iode et de brome, sont obtenues en multipliant le nombre de ml de complexon III par 25.38 et 15.98, respectivement.

CONCLUSION

Les résultats obtenus avec différentes proportions de bromures et iodures sont satisfaisants. La méthode complexométrique s'est montrée sensiblement plus rapide que la méthode gravimétrique. La méthode décrite sert également pour les microdosages. On utilise dans ce cas une solution de complexon III 0.001 *M* et les facteurs pour l'iode et le brome sont respectivement 0.254 mg et 0.160 mg par ml de réactif.

RÉSUMÉ

La méthode décrite est basée sur celle de Bekk. Dans une première opération, les bromures et les iodures sont précipités à l'aide de nitrate d'argent. Après une seconde précipitation, le bromure et l'iodure d'argent sont oxydés. Le bromure se décompose et le brome se dégage, alors que l'iodure se transforme en iodate. L'iodate est réduit au moyen de sulfite de sodium en iodure d'argent qui précipite. Les précipités des deux opérations sont dissous dans une solution ammoniacale de tétracyanure de nickel. L'argent forme un complexe avec le cyanure et libère le nickel qui est dosé par voie complexométrique. Ainsi les bromures et les iodures sont déterminés indirectement. La méthode donne des résultats très satisfaisants et est assez rapide. Elle peut être utilisée pour les microdosages de bromures et d'iodures.

SUMMARY

Bromides and iodides are determined simultaneously by precipitation as silver halide. In another aliquot, silver halides are oxidized, bromine being liberated; the iodate formed is then reduced to iodide which precipitates. The silver precipitates are treated with ammoniacal tetracyano nickelate and displaced nickel is determined complexometrically. Bromide is determined by difference.

ZUSAMMENFASSUNG

Es wird eine komplexometrische Methode zur Bestimmung von Bromid und Jodid im Gemisch beschrieben. Nach Fällung mit Silbernitrat wird die Summe von Silberbromid und -jodid komplexometrisch bestimmt. Eine zweite Fällung der beiden Halogenide wird mit Bichromat–Schwefelsäure oxydiert. Nach Vertreibung des Broms wird das Jodat reduziert, wobei Silberjodid

ausfällt. Der abgetrennte Silberjodidniederschlag wird nach Zugabe von Tetracyanonickelat mit Komplexonlösung titriert. Der Bromidgehalt wird aus der Differenz der beiden Titrationen errechnet.

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DOSAGE INDIRECT DU POTASSIUM PAR COMPLEXOMÉTRIE

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Les méthodes gravimétriques pour le dosage du potassium sont relativement longues et délicates. Les sels de potassium doivent être soigneusement séchés et déshydratés avant d'être pesés. Ces deux opérations exigent des soins spéciaux et peuvent durer des heures jusqu'à poids constant. D'autre part, les sels de potassium étant beaucoup plus volatils que les sels correspondants de sodium, il y a toujours le risque de provoquer une volatilisation partielle par un chauffage prolongé.

Ces difficultés[1] nous ont fait recourir à une méthode volumétrique pour le dosage du potassium sous forme de perchlorate.

Le principe réside dans la transformation du perchlorate en chlorure de potassium[2,3] et précipitation du chlorure par le nitrate d'argent. On applique ensuite la méthode complexométrique[4,5] pour le dosage des halogènes, basée sur la mise en liberté de l'ion nickel lorsqu'on ajoute un sel d'argent à une solution de tétracyanure de nickel

$$2AgCl + [Ni(CN)_4]^{-2} \rightarrow 2[Ag(CN)_2]^- + Ni^{+2} + 2Cl^-$$

Le nickel libéré est titré à l'aide du complexon III.

Réactifs

Chlorure d'ammonium (pro analisi); solution de nitrate d'argent à 5%; solution de nitrate d'argent à 0.1%; solution d'acide nitrique à 1%; solution de complexon III 0.1 *M*; solution de murexide, saturée dans l'eau; solution ammoniacale de tétracyanure de nickel 0.1 *M*, préparée par titrage précis d'une solution de sulfate de nickel 0.1 *M* avec une solution de cyanure de potassium *M*, après addition d'ammoniaque (le titrage est terminé lorsque l'indicateur (murexide) vire du jaune au violet).

Mode opératoire

Le précipité de perchlorate de potassium est séché rapidement en le lavant avec un peu d'éther et ensuite enlevé soigneusement du filtre Gooch* et introduit dans une capsule de platine. On ajoute 2 à 3 g (environ 5 fois le poids du précipité) de chlorure d'ammonium et on mélange le tout intimement. On recouvre le mélange avec une couche de chlorure d'ammonium et l'on chauffe doucement pendant une à deux heures après avoir couvert la capsule avec un verre de montre.

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* Pour de petites quantités de potassium, il pourrait être avantageux d'effectuer la précipitation de $KClO_4$ dans un tube à centrifuger.

Au cas où l'on utilise une capsule en porcelaine, il faut ajouter au mélange 1 ml d'acide chloroplatinique. On doit veiller à ce que la température du mélange soit en-dessous du point de fusion du chlorure résiduel (sinon on risque d'attaquer les parois de la capsule de platine). On ajoute encore du chlorure d'ammonium et l'on chauffe doucement pendant une demi-heure. On laisse refroidir et on dissout les chlorures dans de l'eau distillée contenue dans un bécher. On ajoute de l'acide nitrique, puis on précipite à l'aide de nitrate d'argent à 5%. On porte le contenu du bécher à l'ébullition pendant 5 min en prenant soin de couvrir le bécher avec un verre de montre.

On refroidit la solution et l'on filtre sur un gooch. Le précipité est lavé avec une solution de nitrate d'argent à 0.1% et ensuite avec l'acide nitrique à 1%. Le filtre est introduit dans un bécher contenant la solution ammoniacale de tétracyanure de nickel. On chauffe doucement en agitant jusqu'à dissolution complète du précipité. On ajoute quelques gouttes d'indicateur et l'on titre le nickel libéré avec la solution de complexon III, jusqu'à ce que la couleur de la solution vire au violet. Pour connaître la quantité de potassium en mg, il faut multiplier le nombre de ml de complexon 0.1 *M* par 7.820 et pour obtenir K_2O par 9.420.

RÉSULTATS ET CONCLUSIONS

Les résultats obtenus par la méthode que nous venons de décrire sont très satisfaisants. Au premier abord, la technique adoptée paraît compliquée et très longue. En effet, il s'agit de traiter deux précipités et avoir recours à une voie indirecte pour déterminer la teneur en potassium. Toutefois, l'expérience nous a montré que la méthode gravimétrique est tout aussi longue et plus délicate. Les écarts maxima sont de l'ordre de 1% sur les valeurs obtenues par gravimétrie.

RÉSUMÉ

Une méthode indirecte par voie complexométrique est décrite pour le dosage du potassium. Le précipité de perchlorate de potassium obtenu par la technique habituelle, est chauffé avec du chlorure d'ammonium pour réduire le perchlorate en chlorure. Le chlorure est dissous dans l'eau et précipité sous forme de chlorure d'argent. Ce précipité est ensuite dissous dans le tétracyanure de nickel. L'argent déplace le nickel et ce dernier est dosé par voie complexométrique.

SUMMARY

An indirect complexometric method for the determination of potassium is described. Potassium is precipitated as perchlorate, which is reduced to chloride. Silver chloride is treated with tetracyano nickelate, nickel being titrated chelatometrically.

ZUSAMMENFASSUNG

Beschreibung einer indirekten komplexometrischen Bestimmung von Kalium. Dieses wird als Kaliumperchlorat gefällt, zu Chlorid reduziert und als Silberchlorid in Gegenwart von Tetracyanonickelat mit Komplexonlösung titriert. Der Umrechnungsfaktor für Kalium wird angegeben.

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COMPLEXOMETRIC AND ARGENTOMETRIC TITRATIONS USING CHEMILUMINESCENT INDICATORS

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We have already described[1,2] some new analytical applications of the chemiluminescent indicators siloxene and luminol (aminophthalic acid hydrazide) which were recommended by KENNY AND KURTZ[3]. We have shown that lophine (2,4,5-triphenylimidasole)[4] and lucigenin (dimethyl-diacrydilium-dinitrate)[5,6] are also suitable indicators for some titrations; the end-points are again based on the appearance or disappearance of chemiluminescent light. Lucigenin seems to be especially suitable owing to its adaptability and reversibility.

There is an essential difference between the mechanism of chemiluminescence of lucigenin and luminol. Both indicators emit light in alkaline media. However, luminol emits the light with various oxidizing agents provided that catalysts are present, whereas, lucigenin emits only with hydrogen peroxide.

We established that in the chemiluminescent mechanism of luminol the hydroxyl free radicals which are formed by the interaction of the catalyst play an important role. Lucigenin needs no free radicals for chemiluminesce. Thus luminol seems to be suitable for the detection of hydroxyl free radicals.

To investigate this problem we first studied the mechanism of decomposition of hydrogen peroxide in alkaline media[7]; we found that the decomposition in the presence of metal hydroxides proceeds mainly by a chain reaction through hydroxyl free radicals according to the Haber-Weiss mechanism[8]. Hence, in a hydrogen peroxide solution containing a catalyst hydroxyl free radicals are formed in almost all cases.

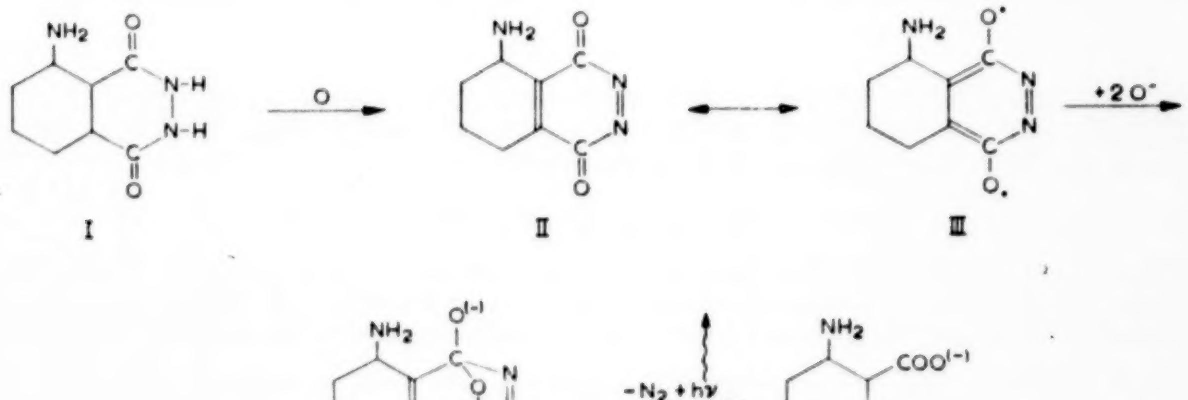

Fig. 1. Chemiluminescent mechanism of luminol.

In a strongly alkaline, catalyst-free media, the kinetics of the autodecomposition of hydrogen peroxide are quite different. In this case perhydroxyl ions, formed by the dissociation of hydrogen peroxide, react with the undissociated hydrogen peroxide molecules forming an unstable complex, which decomposes on collision with the wall of the vessel or with a molecule which can take up the energy. We found that lucigenin takes up this energy from the unstable perhydroxyl complex and thus catalyses the decomposition of hydrogen peroxide. The transferred energy is then emitted by the lucigenin molecule as chemiluminescent light, which has the same spectral composition, as its fluorescent light. Lucigenin is regenerated at the same time.

With this decomposition mechanism of hydrogen peroxide in relation to our previous investigations, we consider that the chemiluminescent mechanism of *luminol* is as shown in Fig. 1.

The chemiluminescent reaction starts with the oxidation of aminophthalic acid hydrazide (I) to the red coloured quinone (II). The mesomer partner of this quinone, the biradical (III), reacts with hydroxyl or oxygen free radicals, which are produced by the oxidizing agents, forming the transannular peroxide (IV). This unstable product loses nitrogen and emits light with simultaneous spin compensation. The end-product of the reaction is aminophthalic acid (V). The reaction is irreversible, because nitrogen splits off more easily than oxygen in the decomposition of the transannular peroxide (IV). The chemiluminescent reaction is thus started in the case of luminol by hydroxyl or oxygen free radicals.

With regard to the chemiluminescent mechanism of *lucigenin*, a blue light is emitted as well as a green luminescent light when a catalyst, *e.g.* heavy metal ions, is present. This blue light is spectrally the same as the fluorescent light of methylacridone, which is the oxidized product of lucigenin; it disappears quickly and the

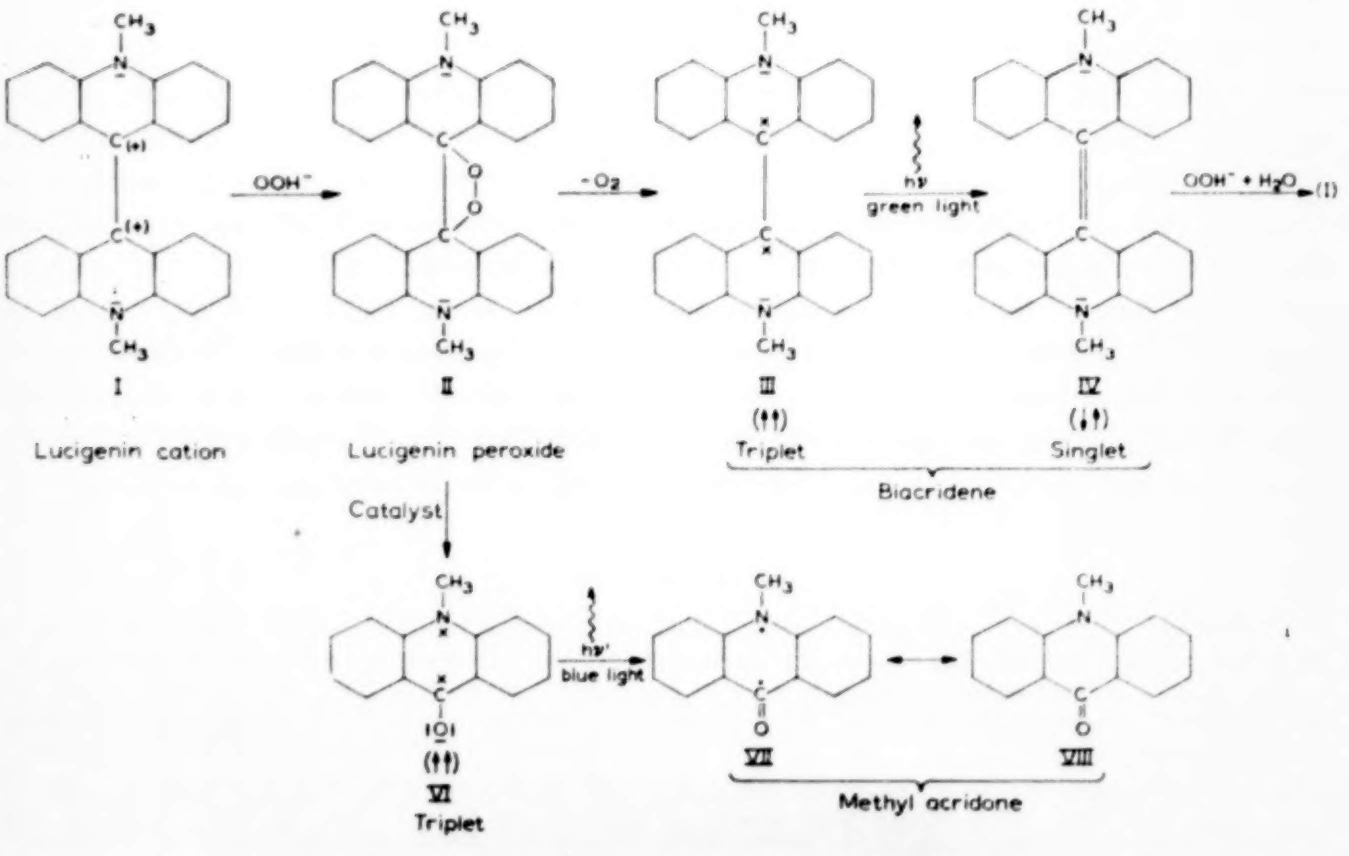

Fig. 2. Chemiluminescent mechanism of lucigenin.

reaction is irreversible. Lucigenin thus emits a green light in alkaline media without catalysts for a long time, and the emittance can be reproduced by further additions of hydrogen peroxide; but in the presence of a catalyst the molecule splits into two parts, the blue chemiluminescent light appears and the reaction becomes irreversible.

We established by polarographic methods that lucigenin forms with hydrogen peroxide a loose complex which takes up four electrons on reduction.

We therefore suggest the mechanism shown in Fig. 2 for the chemiluminescence of lucigenin. The lucigenin cation (I) forms lucigenin peroxide (II) with perhydroxyl ions. This molecule loses oxygen at a relatively low activation energy (20–25 cal.) and forms an excited molecule, the biacridene (III), which has a triplet electron system. This emits a green light by spin compensation. The biacridene (IV) is oxidized by a new perhydroxyl ion to the lucigenin cation (I), and the cycle is then repeated. According to this mechanism lucigenin may be regarded as a catalyst for peroxide decomposition, transforming the energy of the reaction into light, while regenerating itself. The fact that lucigenin emits light very steadily for a long time until the hydrogen peroxide is consumed can thus be explained. Water plays an important part in the last reaction step. We established that in carbon tetrachloride containing pyridine or in benzene, neither lucigenin nor the biacridene emits light with water-free hydrogen peroxide. When water is added to these systems chemiluminescence occurs immediately. This makes it possible to determine the water content of organic solvents by a photometric method.

In the presence of catalysts an irreversible reaction also occurs. The catalyst decomposes the lucigenin peroxide and the methylacridone (VI) is formed in an excited state. This emits a blue chemiluminescent light by spin compensation. The methylacridone, in the ground state, is an inactive end-product.

It is possible to use chemiluminescent indicators for the complexometric determination of copper(II). The sodium salt of EDTA stabilizes the hydrogen peroxide solution, because it forms complexes with the copper(II) (and other heavy metal ions) which catalyse the decomposition. In an alkaline solution containing the copper(II)–EDTA luminol shows no chemiluminescence because there are no hydroxyl free radicals present. Lucigenin however emits light steadily, because it does not require hydroxide free radicals for chemiluminesce. When an ammoniacal copper(II) solution is titrated in the presence of luminol with an EDTA solution containing 0.01% hydrogen peroxide, the mixture emits light until an excess of copper(II) is present. At the equivalence point the light disappears. If the titration is carried out in the presence of lucigenin, there are short flashes of light before the equivalence point is reached but steady chemiluminescence appears only when all the copper has been titrated and hydrogen peroxide no longer decomposes.

EXPERIMENTAL

Stock solutions. 0.01 *M* Copper(II) sulphate solution: 2.4969 g of pro analysi $CuSO_4 \cdot 5H_2O$ was dissolved in 1 l of water. Its copper content was checked by electrogravimetric measurements.

0.01 *M* lead nitrate solution: To 3.3123 g of pro analysi $Pb(NO_3)_2$ 1 ml of 2 *N* nitric acid was added, and the mixture was made up with water to 1 l. Its lead content was checked gravimetrically as lead sulphate.

0.01 *M* mercury(II) nitrate solution: 1.2 g of yellow mercuric oxide was dissolved in 5 ml of 1 : 1 nitric acid, and the mixture was made up with water to 1 l. The mercury content was determined by Volhard's method.

0.1 *N* silver nitrate solution: 16.9888 g of pro analysi $AgNO_3$ was dissolved in 1 l of water.

0.1 N potassium iodide solution: 16.6014 g of KI was dissolved in 1 l of water; the iodide content was measured argentometrically in the presence of Variamine Blue indicator[9].

Standard solution. 0.02 M EDTA solution: 3.8 g of Na_2-EDTA was dissolved in water and diluted to 0.5 l. It was standardized against standard magnesium sulphate solution. 0.01 M solution was prepared by dilution of this solution. The 0.01 M solution containing hydrogen peroxide which was required for titrations of copper(II) was mixed per litre with 20.0 ml of 3% hydrogen peroxide before dilution. The normality of this solution decreased by 0.5% weekly.

Indicators. 1) 0.5% lucigenin: 1.0 g of lucigenin was dissolved with slight heating in 200 ml of water. 2) 0.01% luminol: 0.1 g of luminol was dissolved in a mixture of 500 ml of water and 5 ml of 1 N sodium hydroxide, and, after complete dissolution, the mixture was diluted to 1 l.

PROCEDURES

1. *Determination of copper(II)*

Add to the test solution 20 ml of 4 N ammonium hydroxide and 1 ml of 0.5% lucigenin or 3 ml of 0.01% of luminol solution. Heat to 90°. Titrate with 0.01 M EDTA containing hydrogen peroxide in the dark. The end-point is indicated by the occurrence of a steady chemiluminescent light in the case of lucigenin or by the disappearance of the light in the case of luminol.

TABLE I

DETERMINATION OF COPPER(II)

0.01 M $CuSO_4$ taken ml	*0.01 M EDTA used ml (mean of 3 titrations)*	*Difference*	
		ml	%
In presence of lucigenin			
5.00	5.02	+0.02	+0.4
9.96	10.01	+0.05	+0.5
20.00	20.01	+0.01	+0.13
50.04	49.97	−0.07	−0.15
In presence of luminol			
5.00	5.02	+0.02	+0.4
9.96	9.96	±0.0	±0.0
20.00	20.03	+0.03	+0.15
50.04	49.90	−0.14	−0.3

The reproducibility of the method is shown in Table I. The standard deviations, calculated from 12 parallel titrations of 20 ml of 0.01 M cupric sulphate, were ± 0.028 ml (± 0.14%) when lucigenin was used, and ± 0.032 ml (± 0.16%) when luminol was used.

Notes

Luminol gives an indicator error of + 0.06 ml (the data in Table I have been corrected). It is advantageous that the determination can be carried out even in the presence of silver ions. Strong oxidizing agents and ions which form stable complexes with EDTA, naturally interfere.

Micro-scale determinations. Place the solution containing 6–720 µg of copper in a 5-ml titration vessel, add 1.0 ml of 4 N ammonium hydroxide and 0.5 ml of luminol indicator, heat to boiling and titrate with a suitable 0.01 or 0.001 M EDTA solution containing hydrogen peroxide from a micro buret in a dark room until chemiluminescence disappears. The accuracy of the micromethod is shown in Table II.

TABLE II

MICRO-DETERMINATION OF COPPER(II)

0.01 M $CuSO_4$ taken ml	*0.01 M EDTA used ml (mean of 3 titrations)*	*Cu calculated µg*	*Cu found µg*	*Difference*	
				µg	*%*
0.100	0.099	63.5	62.4	— 1.1	— 1.7
0.200	0.197	127.1	125.2	— 1.9	— 1.5
0.500	0.495	317.7	314.6	— 3.1	— 1.0
1.000	0.980	635.4	622.3	—13.1	— 2.1
0.001 M $CuSO_4$ taken ml	*0.001 M EDTA used ml (mean of 3 titrations)*	*Cu calculated µg*	*Cu found µg*	*Difference*	
				µg	*%*
0.100	0.115	6.4	7.3	+ 0.9	+15.0
0.200	0.203	12.7	12.9	+ 0.2	+ 1.6
0.500	0.499	31.8	31.7	— 0.1	— 0.2
1.000	0.992	63.5	63.0	— 0.5	— 0.8

2. *Determination of EDTA*

The first procedure can be carried out in the reverse direction. To the *ca.* 0.01 *M* EDTA solution add 20 ml of 4 *N* ammonium hydroxide, 1 ml of 3% hydrogen peroxide and 3 ml of luminol or 1 ml of lucigenin indicator. Heat the solution to 90° and titrate in the dark with a standard copper(II) sulphate solution. The end-point is indicated in the case of lucigenin by the disappearance of the light; with luminol a green light appears. The method, as is shown by the data in Table III, is suitable for the standardization of EDTA solutions. The standard deviations, calculated from 12 parallel titrations of 20 ml of 0.01 *N* EDTA, were ± 0.026 ml (± 0.13%) when lucigenin was used. The difference between the mean and true values was —0.1%. With luminol these deviations were ± 0.034 ml (± 0.17%) and —0.2% respectively.

TABLE III

DETERMINATION OF EDTA

0.01 M EDTA taken ml	*0.01 M $CuSO_4$ used ml (mean of 3 titrations)*	*Difference*	
		ml	*%*
In presence of lucigenin			
5.00	5.02	+0.02	+0.4
9.96	9.93	—0.03	—0.3
20.00	19.99	—0.01	—0.05
50.04	49.93	—0.11	—0.2
In presence of luminol			
5.00	4.96	—0.04	—0.8
9.96	9.97	+0.01	+0.1
20.00	19.96	—0.04	—0.2
50.04	49.97	—0.07	—0.14

3. *Determination of lead and mercury(II) ions*

The titration of EDTA with a copper(II) solution makes possible the determination of ions which form a stable complex with EDTA in ammoniacal media; excess of EDTA can be back-titrated in the presence of luminol or lucigenin with a standard copper(II) sulphate solution.

Procedure

To the *ca.* 0.01 *M* lead or mercury(II) nitrate solution add a known excess of standard 0.01 *M* EDTA. Heat the solution to boiling, add 20 ml of 4 *N* ammonium hydroxide, 1 ml of 3% hydrogen peroxide and finally 3 ml of luminol or 1 ml of lucigenin indicator. Titrate the mixture in the dark with a standard copper(II) sulphate solution. At the equivalence point the solution containing lucigenin ceases to light, while in the presence of luminol the dark solution begins to emit chemiluminescence.

TABLE IV

DETERMINATION OF LEAD

0.01 *M* $Pb(NO_3)_2$ taken ml	0.01 *M* EDTA added in excess ml	0.01 *M* $CuSO_4$ used ml (mean of titrations)	0.01 *M* $Pb(NO_3)_2$ found ml	Difference	
				ml	%
In presence of lucigenin					
5.00	25.00	20.02	5.02	+0.02	+0.4
9.96	30.00	20.00	9.96	±0.0	±0.0
20.00	40.00	19.96	19.96	—0.04	—0.2
30.00	50.00	20.02	30.02	+0.02	+0.1
In presence of luminol					
5.00	25.00	20.00	5.00	±0.0	±0.0
9.96	30.00	20.04	10.00	+0.04	+0.4
20.00	40.00	20.00	20.00	±0.0	±0.0
30.00	50.00	20.04	30.04	+0.04	+0.1

TABLE V

DETERMINATION OF MERCURY(II) IN PRESENCE OF LUMINOL

0.01 *M* $Hg(NO_3)_2$ taken ml	0.01 *M* EDTA added ml	0.01 *M* $CuSO_4$ used ml (mean of 3 titrations)	0.01 *M* $Hg(NO_3)_2$ found ml	Difference	
				ml	%
5.06	20.00	14.95	5.05	—0.01	—0.2
10.11	30.00	19.85	10.15	+0.04	+0.4
20.23	49.90	29.58	20.32	+0.09	+0.5
30.34	49.90	19.63	30.27	—0.07	—0.2

Table IV shows the results of determinations of lead with lucigenin or luminol indicator, while Table V gives mercury(II) determinations with luminol. Precision and accuracy data computed from 12 titrations of 20 ml of 0.01 *M* solutions are as follows. The standard deviation of the determination of lead was ± 0.05 ml (± 0.25%) the difference between the mean and true value being —0.1%. The corresponding data for mercury(II) determinations were ± 00.4 ml (± 0.21%) and —0.05% respectively.

4. *Argentometric determination of iodide ions*

Lucigenin can be used as a chemiluminescent indicator for argentometric titrations of iodide ions. It is absorbed in an ammoniacal media on the surface of the negative

TABLE VI

DETERMINATION OF IODIDE

0.1 N KI taken ml	*0.1 N $AgNO_3$ used ml (mean of 3 titrations)*	*Difference*	
		ml	%
5.00	5.03	+0.03	+0.6
9.96	9.94	—0.02	—0.2
20.00	20.02	+0.02	+0.1
50.04	50.09	+0.05	+0.1

TABLE VII

MICRO-DETERMINATION OF IODIDE

0.1 N KI taken ml	*0.1 N $AgNO_3$ used ml (mean of 3 titrations)*	*mg I^-*		*Difference*	
		calculated	*found*	*mg*	%
0.100	0.112	1.27	1.41	+0.14	+12
0.200	0.207	2.54	2.61	+0.7	+ 3.5
0.500	0.503	6.35	6.39	+0.04	+ 0.6
1.000	0.993	12.69	12.60	—0.09	— 0.7

TABLE VIII

INTERFERENCE OF FOREIGN IONS IN THE TITRATION OF IODIDE

(In all cases 20.00 ml of 0.1 *N* KI was taken)

Foreign ion	*0.1 N $AgNO_3$ used ml (mean of 3 titrations)*	*Difference*		*Remarks*
		ml	%	
Cl^-	20.03	+0.03	+ 0.15	Clear end-point
Br^-	20.12	+0.12	+ 0.6	
CN^-	30.09	+10.09	+50.5	Solution emits light till 11.10 ml of $AgNO_3$ is consumed, but becomes dark when AgI is precipitated. At the end-point it looks like an I^- solution when CN^- ions are not present
SCN^-	26.80	+6.80	+34.0	Light disappears slowly when $AgNO_3$ is added. At the end-point a very slight light can be seen
$C_2O_4^{-2}$	20.07	+0.07	+ 0.3	Clear end-point
PO_4^{-3}	20.43	+0.43	+ 2.15	Clear end-point
$[Fe(CN)_6]^{-4}$	20.68	+0.68	+ 3.4	Light is less at the end-point than it is when only I^- ions are present
$[Fe(CN)_6]^{-3}$				No light since $Fe(CN)_6^{-3}$ oxidizes H_2O_2
CrO_4^{-2}	23.33	+3.33	+16.6	A very little light appears at the end-point

charged silver iodide precipitate and thus does not emit light even in the presence of hydrogen peroxide; when the charge on the surface of the precipitate is changed, lucigenin is desorbed and the solution suddenly luminesces.

Procedure

To the solution to be examined add 10 ml of 4 *N* ammonium hydroxide, 1 ml of lucigenin indicator and 1 ml of 0.3% hydrogen peroxide. Titrate the mixture in a dark room until chemiluminescent light appears suddenly and steadily.

Note

Tables VI and VII show that the method is suitable for macro and micro determinations of iodide. It is advantageous that the titration can be carried out even in the presence of chloride and bromide ions, the silver salts of which are soluble in ammonium hydroxide. When cyanide and iodide ions are present, they are titrated together. Thiocyanates and complex-forming ions interfere. The results of titrations carried out in the presence of other ions are shown in Table VIII. The standard deviation of the method, calculated from 12 titrations of 20 ml of 0.1 *M* potassium iodide, was ± 0.032 ml (± 0.16%); these was no difference between the mean and true value.

Chemiluminescent indicators are very useful when the solution to be examined is turbid, opaque or dark and the usual dye-indicators cannot be used.

SUMMARY

Lucigenin and luminol are suitable chemiluminescent indicators for complexometric and argentometric titrations. The mechanisms of chemiluminescence of these indicators are quite different. Methods are given for the determination of copper(II), lead and mercury(II) ions and for the standardization of EDTA solutions. Lucigenin is suitable as an adsorption indicator for the argentometric determination of iodide ions, even in the presence of chloride and bromide.

RÉSUMÉ

La lucigénine et le luminole sont proposés comme indicateurs pour les titrages complexométriques et argentométriques. Des méthodes ont été établies pour le dosage du cuivre, du plomb et du mercure ainsi que pour l'étalonnage de solution de complexon(III). La lucigénine peut être utilisée comme indicateur d'adsorption pour le dosage argentométrique des iodures, même en présence de chlorures et de bromures.

ZUSAMMENFASSUNG

Lucigenin und Luminol eignen sich als chemiluminescente Indikatoren bei komplexometrischen und argentometrischen Titrationen. Es werden Methoden beschrieben zur Bestimmung von Kupfer, Blei und Quecksilber sowie zur Einstellung von Komplexon(III) Lösungen. Lucigenin kann ferner als Adsorptionsindikator bei der Titration von Jodid, auch in Gegenwart von Chlorid und Bromid, verwendet werden.

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THE HETEROMETRIC DETERMINATION OF PLATINUM, PALLADIUM AND GOLD BY TITRATION WITH PHENANTHROLINE

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INTRODUCTION

The reactions of platinum, palladium and gold chlorides with phenanthroline in chloride or thiocyanate solution have already been studied heterometrically[1]. The various compounds obtained have been discussed.

The present report deals with the actual determinations of the metals singly and in mixtures. We have already shown that the sensitivity of the phenanthroline-noble metal reaction is lower than that with other specific and complex nitrogen compounds. (A study with papaverine will be presented later). However, the sensitivity is often not the decisive criterion of the importance of a heterometric reaction. Thus, phenanthroline presents a series of heterometric reactions and compounds which can be applied successfully for the precise, direct determination of all the metals present in mixtures without any previous separations whatsoever.

The importance of the proposed methods is that two or three noble metals in an alloy (or in a solution of chlorides) can be determined from the critical points of one titration curve only, *i.e.* two noble metals, forming different insoluble compounds can both be determined accurately from the same heterometric curve.

The simultaneous determination of platinum and palladium or gold and palladium required only 2 mg of alloy; the determination of gold and platinum required at least double this amount. Generally the third noble metal present could be determined from the difference. The determination of all three metals in an alloy or in a soluble mixture of chlorides was possible in several ways by two separate heterometric titrations. A titration lasted about 10–15 min at 20°. In almost all cases studied, the second end-point (↓↓) agreed exactly with the theoretical sum of the amounts of metals determined. Some errors occurred at the last analytical intersection point (↓) (first end-point), but these could be avoided by practise.

EXPERIMENTAL

The same reagents and working conditions were used as in previous reports[2,3].

RESULTS

Table I describes a series of heterometric titrations of mixtures, chiefly of two metals, with phenanthroline. The course of a few titrations is also shown in Fig. 1. Before the different methods for the determination of the metals are indicated, the working principles and the results are discussed.

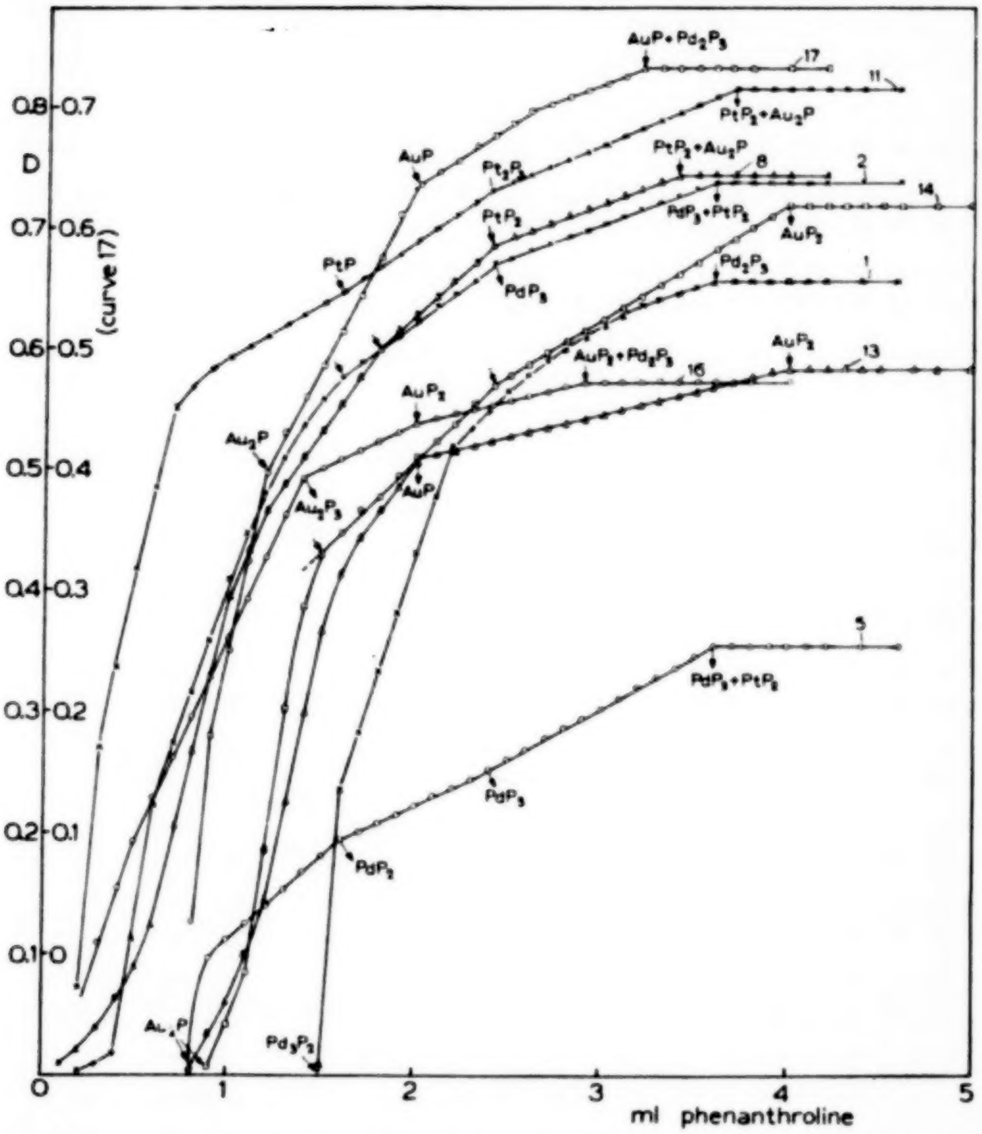

Fig. 1. Titrations of mixtures of platinum, palladium and gold halides with phenanthroline.

In the case of platinum, it is possible to keep the platinum dissolved or to determine the platinum simultaneously with one of the two other noble metals present. Probably any quantity of platinum could remain dissolved in chloride solution at pH 1–7, or in thiocyanate solution at about pH 7. Palladium and gold were both precipitated either in chloride or thiocyanate solutions at pH 1–7. Therefore, if both are present, they can only be determined from two different critical points of the titration curve. The platinum was precipitated from acid thiocyanate solution only, thus the insoluble platinum thiocyanate compound could also be determined from an intersection point of the same curve.

In all the cases given, only those metal-phenanthroline compounds which functioned as *final* compounds (↓↓) were of analytical value if the single metal analysed was titrated under the same working conditions.

The presence of chloride in large excess seemed to have no influence on the results. The influence of the concentration of the thiocyanate varied. Generally (especially

TABLE I

General composition: *a* ml reagents + (10—*a*) ml H_2

Expt. No.	Composition	%/mg metal Pt	 Pd	 Au	Molarity of P
1	3 ml 0.004 M H_2PtCl_6 + 3 ml 0.004 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M NaCl	64.7% 2.3427	35.3% 1.2804		0.005
2	3 ml 0.002 M H_2PtCl_6 + 4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 1 ml 0.25 M KCNS	57.8% 1.1714	42.2% 0.8536		0.01
3	3 ml 0.002 M H_2PtCl_6 + 4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml 0.25 M KCNS	57.8% 1.1714	42.2% 0.8536		0.01
4	3 ml 0.002 M H_2PtCl_6 + 4 ml 0.002 M $PdCl_2$ + 1 ml 3 M HNO_3 + 2 ml 0.25 M KCNS	57.8% 1.1714	42.2% 0.8536		0.01
5	3 ml 0.002 M H_2PtCl_6 + 4 ml 0.002 M $PdCl_2$ + 1 ml M HNO_3 + 2 ml M KCNS	57.8% 1.1714	42.2% 0.8536		0.01
6	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3	37.3% 2.3427		62.7% 3.9440	0.005
7	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml 3 M HNO_3	37.3% 2.3427		62.7% 3.9440	0.005
8	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.25 M KCNS	37.3% 2.3427		62.7% 3.9440	0.01
9	3 ml 0.004 M H_2PtCl_6 + 5 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3 + 1 ml 0.25 M KCNS	32.2% 2.3427		67.8% 4.9300	0.01
10	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	37.3% 2.3427		62.7% 3.9440	0.01
11	4 ml 0.004 M H_2PtCl_6 + 2 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3 + 2 ml 0.5 M KCNS	61.3% 3.1236		38.7% 1.9720	0.01
12	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M Na-acetate + 1 ml 0.25 M KCNS	37.3% 2.3427		62.7% 3.9440	0.01
13	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M Na-acetate + 1 ml 0.25 M KCNS	37.3% 2.3427		62.7% 3.9440	0.01
14	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M Na-acetate + 1.5 ml 0.5 M KCNS	37.3% 2.3427		62.7% 3.9440	0.01
15	3 ml 0.004 M H_2PtCl_6 + 4 ml 0.005 M $HAuCl_4$ + 1 ml M Na-acetate + 1.5 ml M KCNS	37.3% 2.3427		62.7% 3.9440	0.01
16	3 ml 0.002 M $PdCl_2$ + 4 ml 0.0025 M $HAuCl_4$ + 1 ml M Na-acetate + 2 ml 0.25 M KCNS		24.5% 0.6402	75.5% 1.9720	0.01
17	3 ml 0.004 M H_2PtCl_6 + 2 ml 0.004 M $PdCl_2$ + 4 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3	32.8% 2.3427	12% 0.8536	55.2% 3.9440	0.01
18	3 ml 0.004 M $PdCl_2$ + 4 ml 0.0025 M $HAuCl_4$ + 1 ml M Na-acetate + 1 ml 0.5 M KCNS		39.3% 1.2804	60.7% 1.9720	0.01
19	4 ml 0.004 M $PdCl_2$ + 3 ml 0.0025 M $HAuCl_4$ + 1 ml M Na-acetate + 1 ml 0.5 M KCNS		53.5% 1.7072	46.5% 1.4790	0.01
20	3 ml 0.005 M H_2PtCl_6 + 3 ml 0.004 M $PdCl_2$ + 3 ml 0.005 M $HAuCl_4$ + 1 ml M HNO_3	40.8% 2.9284	18.0% 1.2804	41.2% 2.9580	0.01
21	3 ml 0.005 M H_2PtCl_6 + 3 ml 0.004 M $PdCl_2$ + 3 ml 0.0025 M $HAuCl_4$ + 1 ml M Na-acet. + 1 ml 0.5 M KCNS	51.4% 2.9284	22.5% 1.2804	26.1% 1.4790	0.01

x = Corning yellow filter (3484); c = contact point; h = horizontal maximum density line; i = intersec

TABLE I

– *x* ml *M b* phenanthroline (= *P*) T = 20°

Found				*End-point*				*Titration time in min*
Initial ppt.		*Intermediates*						
at ml P	*compound formed*	*ml of P used*	*Compounds obtained*	*at ml P*	*Compounds obtained*	*Optical density value*	*% error*	
1.6	$Pd_3P_2\uparrow$			i 3.60 h	$Pd_2P_3\downarrow\downarrow$	0.66	0.0	12
0.4		c 1.6; 2.4	$PdP_2\downarrow \rightarrow PdP_3\downarrow\downarrow$	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.74	0.0	15
0.6		2.5	$PdP_3\downarrow\downarrow$	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.50	0.0	12
0.4		c 2.0 (?)	$PdP_3\downarrow\downarrow$ (?)	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.52	0.0	15
0.9	$PdP\uparrow$	1.6; 2.4	$PdP_2\downarrow \rightarrow PdP_3\downarrow\downarrow$	i 3.60 h	$PdP_3\downarrow\downarrow + PtP_2\downarrow\downarrow$	0.36	0.0	14
1.1	$Au_4P\uparrow$	2.5	$Au_3P_2\downarrow$	i 4.00 h	$AuP\downarrow\downarrow$	0.49	0.0	13
1.2	$\sim Au_4P\uparrow$	c ~1.9; 2.6	$Au_2P\downarrow \rightarrow Au_3P_2\downarrow$	i 4.00 h	$AuP\downarrow\downarrow$	0.41	0.0	14
0.2		1.8; 2.4	$Pt_2P_3\downarrow \rightarrow PtP_2\downarrow\downarrow$	i 3.40 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.75	0.0	12
0.3		c 1.0; 1.75; 2.4	$\sim PtP\downarrow \rightarrow Pt_2P_3\downarrow \rightarrow PtP_2\downarrow\downarrow$	i 3.70 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.76	0.0	11
0.2		c 1.9	$Pt_2P_3\downarrow$	i 3.40 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.76	0.0	12
0.1		1.6; 2.4	$PtP\downarrow \rightarrow Pt_2P_3\downarrow$	i 3.70 h	$PtP_2\downarrow\downarrow + Au_2P\downarrow\downarrow$	0.82	0.0	12
1.0	$Au_2P\uparrow$	2.0; ~2.9	$AuP\downarrow \rightarrow Au_2P_3\downarrow$	i 4.00 h	$AuP_2\downarrow\downarrow$	0.46	0.0	12
0.9	$Au_2P\uparrow$	2.0	$AuP\downarrow$	i 4.00 h	$AuP_2\downarrow\downarrow$	x0.59	0.0	11
1.0	$Au_2P\uparrow$	c 1.5; 2.40	$Au_4P_3\downarrow \rightarrow Au_4P_5\downarrow$	i 4.00 h	$AuP_2\downarrow\downarrow$	0.72	0.0	12
0.8				i 4.00 h	$AuP_2\downarrow\downarrow$	0.32	0.0	17
0.2		1.4; 2.0	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 2.90 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.57	0.0	14
0.8	$Au_2P\uparrow$	1.2; 2.0	$Au_2P\downarrow\uparrow \rightarrow AuP\downarrow\downarrow$	i 3.20 h	$AuP\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.74	0.0	13
0.0		1.44; 2.01	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 3.80 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.93	0.0	13
0.0		1.0; 1.47	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 3.90 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.91	0.0	14
0.7		1.54; 2.02	$AuP\downarrow\downarrow$	i 3.30 h	$AuP\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.78	0.0	13
0.2		1.1; 1.50	$Au_2P_3\downarrow \rightarrow AuP_2\downarrow\downarrow$	i 3.30 h	$AuP_2\downarrow\downarrow + Pd_2P_3\downarrow\downarrow$	0.84	0.0	13

on point.

at about pH 1) there was an optimum concentration of thiocyanate in each case. An excess of thiocyanate decreased the maximum optical density values, although the composition of the final compound usually remained unchanged. Large amounts of acid also had an adverse effect on the determination. Thus the best results for platinum and palladium (Expts. 2–5, Table I) were obtained with a minimum quantity of thiocyanate, although below a certain level of thiocyanate the results become uncertain. In the determination of platinum and gold (Expts. 8–11) the first end-point (PtP_2) was reliable only if a minimum amount of thiocyanate was used. In the presence of an excess of thiocyanate a different platinum compound was found (Pt_2P_3). In all these cases the maximum optical density value remained the same (Expts. 8–10). In acetate solutions (Expts. 12–15), the platinum always remained dissolved. The final gold compound was always of the same composition (AuP_2), but the intermediates traced were different if more thiocyanate was used. The optimum quantity of thiocyanate seemed to be somewhat larger than usual in these experiments (Expt. 14). The ratio of the metals in the test solution could also influence the result; we did not examine this further.

TABLE II

pH	*R⁻*	*Metals present*	*Metals determined as*	*Approx. mg metal analyzed*
1	Cl^-	Pt, Pd	Pd_2P_3	3.5
1	CNS^-	Pt, Pd	PdP_3 (1), PtP_2 (2)	2
1	Cl^-	Pt, Au	AuP	6
1	CNS^-	Pt, Au	PtP_2 (1), Au_2P (2)	5–6
7	CNS^-	Pt, Au	AuP_2	6
7	CNS^-	Pd, Au	AuP_2 (1), Pd_2P_3 (2)	2.5
1	Cl^-	Pt, Pd, Au	AuP (1), Pd_2P_3 (2)	6–7

Table II summarizes the final compounds obtained. The numbers in brackets show the order of formation of the compounds; this depended on the composition of the test solution. Thus in mixtures of platinum and palladium in thiocyanate solution at about pH 1, the palladium was precipitated first; in mixtures of platinum and gold (under the same conditions), the platinum came first, while in mixtures of gold and palladium in all cases the gold precipitated first. For the determination of a single metal, approximately 1 mg of palladium, 1–2.5 mg of platinum and 2–4 mg of gold were necessary.

METHODS

General remarks

In all the following methods, the error at the first maximum optical density point was always approximately equal to zero. The last intermediate intersection point (↓) was always obtained from the intersection of the two adjacent lines (branches) of the titration curve.

1. *Determination of platinum*

About 3–4 mg of platinum as chloroplatinic acid in 10 ml aqueous solution, containing 1 ml of *M* HNO_3 and 1–2 ml of 0.5 *M* KCNS, are titrated with aqueous

0.01 *M* phenanthroline. The end-point appears at the first maximum optical density point, coinciding with the quantitative formation of Pt_1P_2.

2. *Determination of platinum and palladium*

About 2 mg of the metals, as chlorides, in 10 ml of solution containing 1 ml of *M* HNO_3 and 1 ml of 0.25 *M* KCNS are titrated with aqueous 0.01 *M* phenanthroline. Two critical points are obtained. The first point, which is the last intermediate intersection point, appears when Pd_1P_3 is quantitatively precipitated. The second point coincides with the first maximum optical density point, giving exactly the sum of Pd_1P_3 and Pt_1P_2.

3. *Determination of palladium*

About 1 mg of palladium as chloride in 10 ml of aqueous solution containing 1 ml of *M* HNO_3 and 1 ml of *M* NaCl, is titrated with aqueous 0.005 *M* phenanthroline. The first optical maximum density point coincides exactly with the quantitative formation of Pd_2P_3. The titration can also be carried out at *ca.* pH 7, using 1 ml of *M* Na-acetate instead of the acid. The solution may then contain 1 ml of *M* KCNS instead of the NaCl.

4. *Determination of palladium in platinum*

The procedure is the same as in 3, with chloride solutions.

5. *Determination of gold in platinum*

About 4 mg of gold, as gold chloride, in 10 ml of aqueous solution, containing 1 ml *M* of Na-acetate and 2–3 ml of 0.25 *M* KCNS, are titrated with aqueous 0.01 *M* phenanthroline. The first optical maximum density point coincides exactly with the quantitative precipitation of Au_1P_2.

The same titration can be carried out in acid solution, by replacing the Na-acetate and the KCNS by 1 ml *M* HNO_3. The titrant is then 0.005 *M* phenanthroline. The end-point appears at the quantitative formation of Au_1P_1. The former method is preferable.

6. *Determination of palladium and gold*

About 3 mg of the metals, as chlorides, in 10 ml of aqueous solution, containing 1 ml of *M* Na-acetate and 2 ml of 0.25 *M* KCNS, are titrated with aqueous 0.01 *M* phenanthroline. Two critical points are obtained; the first point (*i.e.* the last intermediate point) coincides with the quantitative formation of Au_1P_2. The second point (*i.e.* the first maximum optical density point) coincides exactly with the quantitative formation of the sum of Au_1P_2 and Pd_2P_3.

7. *Determination of platinum and gold*

About 5 mg of the metals, as chlorides, in 10 ml of aqueous solution, containing 1 ml of *M* HNO_3 and 1 ml of 0.25 *M* KCNS, are titrated with aqueous 0.01 *M* phenanthroline. Two critical points are obtained. The first point (the last intermediate point) coincides with the quantitative formation of Pt_1P_2. The second point (the first maximum optical density point) coincides exactly with the quantitative formation of the sum of Pt_1P_2 and Au_2P_1.

8. *Determination of phenanthroline*

About 4 mg of phenanthroline in 10 ml aqueous solution, containing 1 ml of *M* Na-acetate are titrated with a 0.004 *M* solution of palladium chloride. The end-point, at the first maximum optical density point, coincides with the quantitative formation of Pd_2P_3.

The test solution may contain some sodium chloride. The analysis can also be carried out at about pH 1 in nitric acid solution, but the former method is preferable.

SUMMARY

Platinum(IV), palladium(II) and gold(III), as chlorides, were determined directly in thiocyanate or chloride solutions by heterometric titration with phenanthroline at pH values of 1-7. Two or even three metals could be determined precisely from the critical points of one or two heterometric titration curves. Several methods are presented.

RÉSUMÉ

Plusieurs méthodes sont proposées pour le dosage du platine, du palladium et de l'or, en présence les uns des autres. On procède par titrage hétérométrique en utilisant la phénanthroline comme réactif.

ZUSAMMENFASSUNG

Durch heterometrische Titration mit Phenanthrolin können Platin, Palladium und Gold nebeneinander bestimmt werden.

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THE ACCURATE DETERMINATION OF COBALT

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INTRODUCTION

Primary standards

The analytical chemistry of cobalt has been reviewed recently[1]. A literature survey reveals the use of a wide range of substances as primary standards (Table I) some of which have been critically discussed by YARDLEY[2].

$CoSO_4$. The important question here is whether ignition of the hydrated sulphate to

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the anhydrous form can be carried out without thermal decomposition of the latter. This affects not only the use of $CoSO_4$ as a primary standard but also the analytical method based on finally weighing the cobalt in this form. The extensive literature on the thermal decomposition of $CoSO_4$, much of which is reported in MELLOR[3], gives values ranging from 440° to 900° for the temperature at which decomposition starts.

TABLE I

COBALT PRIMARY STANDARDS

$CoSO_4$	$[Co(NH_3)_4CO_3]NO_3$
$CoSO_4 \cdot 7H_2O$	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_2$	J. M. Cobalt sponge 99.9% pure[a]
$CoCl_2 \cdot 6H_2O$	J. M. Cobalt sheet[a]
$Co(NO_3)_2 \cdot 6H_2O$	Electrolytic cobalt
$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Metallic cobalt (Hydrogen reduced)
$K_3[Co(CN)_6]$	

[a] Johnson Matthey & Co. Ltd., London.

WILLARD AND HALL[4] found 550° as the upper limit for ignition without decomposition, although later WILLARD AND FOWLER[5] prepared the anhydrous sulphate by heating to constant weight at 500°–650°. YARDLEY[2] in assessing the value of $CoSO_4$ as a primary standard found that ignition at 400°–550° always produced a product either containing a trace of water, or deficient in SO_3. In a thermogravimetric study of cobalt sulphate DUVAL[5] concluded that dissociation took place over the whole range 350°–820°. Recently, by means of thermogravimetric and differential thermal analysis OSTROFF AND SANDERSON[6] have reported the relative decomposition temperature as 708°.

$CoSO_4 \cdot 7H_2O$. For accurate work it is questionable whether this substance can be dried without partial decomposition taking place, a difficulty often met in hydrated compounds. DUVAL[5] states that the original substance contains 8.5 molecules of water of crystallisation.

$CoCl_2$ and $CoCl_2 \cdot 6H_2O$. The hexahydrate is sufficiently efflorescent to make its use inadvisable. The anhydrous form is easily made but is too hygroscopic for weighing with certainty.

$Co(NO_3)_2 \cdot 6H_2O$. This is subject to the same disadvantage as the hydrated sulphate.

$[Co(NH_3)_4CO_3]NO_3$; $[Co(NH_3)_5Cl]Cl_2$; $K_3[Co(CN)_6]$. These complexes have many favourable features as primary standards, *e.g.* they may be easily recrystallised and dried. The pyrosulphate fusion required before preparing the standard solution presents no difficulty.

J.M. 99.99% sponge. The product is described as 99.99% pure, excluding gas content, and this has encouraged some recent workers to use it as a primary standard. The manufacturers state that the sponge contains a little unreduced oxide. Clearly, its value will depend on how much is present and the extent to which oxidation takes place on storing it. Cobalt sheet and wire are also available.

Electrolytic cobalt. This has been used as primary standard in many cases. It will be shown in a following paper that electrolytic cobalt is invariably impure, the degree of impurity depending on the procedure used in its preparation.

Metallic cobalt. By this is meant finely divided hydrogen reduced metal similar to the sponge. At lower temperatures the reduction yields a black pyrophoric powder. Metallic cobalt has the same potential defects as the sponge.

Many investigators, for the purpose of assessing particular methods, have standardised cobalt stock solutions of arbitrary strength by using other methods of cobalt analysis. Table II lists the methods which have been used for this purpose.

TABLE II

Electrolytic
Sulphate
α-Nitroso-β-naphthol reduction to metallic cobalt
Anthranilate
Phosphate
EDTA
Ferricyanide
Oxidation by H_2O_2 followed by iodometric procedure

Where a particular method has been used, knowledge of the exact procedure would be required to assess its value, as many methods give erroneous results unless used carefully. The phosphate method provides a striking example of this. KOLTHOFF AND WATERS[7] standardised a cobalt nitrate solution using the method although DUFTY[8] had established that presence of nitrate ion interferes giving low results.

Methods of cobalt analysis have been critically examined and it will be shown* that most of the recommended methods contain unsatisfactory features and are unsuitable for the accurate determination of cobalt.

To summarise, many methods have been used to prepare standard cobalt solutions for assessing methods of analysis. Many involve substances or procedures invalidated by previous work. This, coupled with the fact that primary standards have been ignored by many workers means that apart from relatively few cases where care has been taken, it is doubtful whether great importance can be attached to the degree of accuracy claimed in much of the cobalt analytical literature.

The aim of the present work is to compare, using a reproducible method under strictly controlled conditions, a number of cobalt primary standards, some of which have not hitherto been used for this purpose. In order to standardise conditions as much as possible, quantities of the standard containing about 100 mg of cobalt were taken for each analysis. To compare the actual cobalt content of each standard with the stoichiometric amount it was necessary to employ a precise method of analysis. A form of the phosphate method was eventually used. Owing to the slight solubility of $CoNH_4PO_4 \cdot H_2O$, determination of residual cobalt in the filtrate was carried out by means of the Nitroso-R-salt method.

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* Parts II and III of this paper.

Standard examined

$CoSO_4$; J. M. 99.99% cobalt sponge; $CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$; J. M. spectrographically standardised cobalt wire; $[Co(NH_3)_5Cl]Cl_2$; $K_3[Co(CN)_6]$; $[Co(NH_3)_6]Cl_3$.

EXPERIMENTAL

Weighing. A calibrated set of Baird and Tatlock Series I nickel–chrome alloy weights was used to calibrate all other weights used.

Volumetric glassware. Volumetric flasks and pipettes were calibrated by the usual methods.

pH measurements. These were carried out using a Cambridge meter with glass and saturated calomel electrodes. The instrument was standardised using $M/20$ potassium hydrogen phthalate (pH 4.00) and a sodium phosphate–potassium phosphate buffer solution (pH 6.81 at 18°).

Chemicals. Unless otherwise stated, all chemicals used were of 'AnalaR' quality.

Preparation of standards

$CoSO_4$. The hydrated compound was re-crystallised three times from almost boiling water. The dried crystals were ground up and ignited in an electric furnace at various temperatures between 500° and 550°. The anhydrous sulphate was stored over phosphorus pentoxide.

$K_3[Co(CN)_6]$. The method of preparation was identical with that used by YARDLEY[2].

$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$. Equimolecular amounts of cobalt sulphate and potassium sulphate were mixed and the disulphate re-crystallised three times from hot water. The crystals were washed with a little water and acetone, ground up and dried in vacuo.

$[Co(NH_3)_6]Cl_3$. The ordinary grade material was recrystallised three times from hot water, the crystals being filtered off after cooling in a refrigerator. They were washed with 60% alcohol and dried in vacuo.

$[Co(NH_3)_5Cl]Cl_2$. This was prepared by the method of WILLARD AND HALL[4].

Preparation of stock solutions

Amounts of the various standards were taken such that their solutions contained approximately 100 mg cobalt per 50 ml.

For the complexes, pyrosulphate fusion was necessary. This was done in a long necked 500-ml thick walled bolt head flask heated in a thermomantle. Possible loss by splashing was thus prevented. After heating to dryness twice using 20 ml conc. sulphuric acid for each 5 g complex, the residue in each case was dissolved in water and made up to one litre. The cobalt sponge and wire were first dissolved in nitric acid and then taken to dryness twice with sulphuric acid.

Analytical methods

Phosphate method I: This method is based partly on the analogous method for zinc[9].

To a neutral cobalt solution containing approximately 100 mg cobalt, 5 g ammonium chloride and 10 ml 2 N sodium acetate were added. The total volume was adjusted to 120 ml. The solution was heated on a water bath; when hot, 12 ml 10% ammonium phosphate was slowly added, and the solution stirred occasionally until the precipitate turned violet. The beaker was now removed and left to stand for one hour. The precipitate was filtered (X4 sintered crucible) washed with 1% ammonium phosphate solution which had been adjusted to pH 7.0 and finally with 5 ml 50% alcohol. After drying for about 15 min at 110° it was ignited for one hour at 730° to convert to $Co_2P_2O_7$.

Filtrate analysis: The filtrate and washings from the phosphate method were made up to 500 ml. To 25 ml diluted to 40 ml and containing one drop phenolphthalein, 1:50 HCl was added until colourless and then a few ml in excess. The solution was boiled gently for a few min, 4 ml 50% sodium acetate solution was added, and after further boiling, 4 ml 0.2% nitroso-R-salt solution was introduced. When the colour had developed fully (about 2 min boiling), 2 ml conc. nitric acid was added, the solution boiled for one more minute, and then cooled rapidly. It was made up to 100 ml in a volumetric flask, and the optical density measured using a 4-cm cell, No. 605 Ilford yellow-green filter (peak transmission 545 mμ) and a blank treated similarly.

Notes: (i) A calibration curve was used for which $[Co(NH_3)_5Cl]Cl_2$ had been used as primary standard. (ii) the reported failure of Beer's law at low cobalt concentrations[10] was not encountered probably owing to the procedure used. (iii) in order to ensure that no interference was caused by ammonium or phosphate ions under the analytical conditions, tests were carried out on dilute cobalt solutions of known strength containing these ions. Neither was found to interfere.

In a second series another form of the phosphate method based on a procedure recommended by SCHOELLER[11] was used.

Phosphate method II: To a neutral cobalt solution containing approximately 100 mg cobalt 10 ml conc. HCl and 10 ml 10% ammonium phosphate solution was added. The total volume was adjusted to 150 ml. After heating on a water bath until hot, sufficient 1:1 ammonia was added to cause the precipitate formed to partly dissolve (25 ml approx.). The precipitate was left to stand 1–2 hours, filtered through an X4 sintered crucible, washed with 1% ammonium phosphate solution followed by a little 50% alcohol, and dried at 110°. It was then ignited at 730° and weighed as the pyrophosphate. The filtrate cobalt was estimated as in the previous method.

Both phosphate methods were tested carefully on arbitrary cobalt solutions and were found to give very consistent results.

RESULTS

Reproducibility of phosphate method

Typical batch of six analyses using phosphate method I: found resp.: 104.6, 104.7, 104.6, 104.6, 104.6 and 104.7 mg Co.

DISCUSSION

Although the two phosphate methods give different results for a particular standard, a similar pattern of results is obtained for a series of different standards. In each case $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$ and $K_3[Co(CN)_6]$ give very similar results, the difference being of the same order as the experimental error for the method. The cobalt wire gives slightly higher results, the mixed sulphate much higher, and the sponge lower results.

It was been pointed out that both the phosphate methods of analysis are precise although method I gives high results in relation to II. A comparison of the mean relative error, therefore, indicates whether the actual cobalt content of a particular standard in relation to the stoichiometric amount, is high or low, in comparison with another standard. For example, in Series I, if $[Co(NH_3)_6]Cl_3$ is assumed to have the exact stoichiometric composition, then in relation to it, cobalt sponge I will have a cobalt content of 99.75%. Comparison of standards in this way does not depend on the absolute accuracy of a method but only on its precision; if slightly high or low in an absolute sense, the relative error would remain constant.

TABLE III

ANALYSIS OF STANDARDS

(Series I: phosphate method I used)

Standard		*Cobalt*[a] *taken mg*	*Total cobalt found mg*	*% difference*
$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$	A[b]	97.8	98.5	+0.7
	A	97.8	98.6	+0.8
	B	100.0	101.0	+1.0
	B	100.0	100.9	+0.9
	C	99.6	100.6	+1.0
	C	99.6	100.7	+1.1
$[Co(NH_3)_5Cl]Cl_2$	A	100.1	100.8	+0.7
	A	100.1	100.6	+0.6
	B	99.9	100.5	+0.6
	B	99.9	100.4	+0.5
	C	100.4	100.9	+0.5
	C	100.4	100.8	+0.4
	C	100.4	100.9	+0.5
J. M. sponge I	A	101.0	101.2	+0.2
(as sulphate)	A	101.0	101.2	+0.2
$[Co(NH_3)_6]Cl_3$	A	100.1	100.5	+0.4
	A	100.1	100.6	+0.5
$K_3[Co(CN)_6]$	A	100.2	100.9	+0.7
	A	100.2	100.8	+0.6
	B	100.2	100.7	+0.5
	B	100.2	100.7	+0.5
$CoSO_4$[c]	A	100.1	100.4	+0.3
	A	100.1	100.3	+0.2
	B	99.0	100.0	+1.0
	B	99.0	100.0	+1.0
	C	100.2	100.3	+0.1
	C	100.2	100.3	+0.1

[a] Based on stoichiometric formula of standard.

[b] A, B etc. refer to independent batches of the particular standard.

[c] $CoSO_4$ A, B, and C were prepared from the anhydrous sulphate ignited at 500°, 530°, and 550° respectively.

In relation to the complexes which have the least objectionable features as primary standard, the cobalt sponge would appear to contain unreduced oxide. It is stated to contain an unspecified amount of this, but it is not included in the 99.99% purity value quoted for the product, a figure derived on the basis of spectrographic analysis.

TABLE IV

ANALYSIS OF STANDARDS

(Series II: phosphate method II used)

Standard		*Cobalt taken mg*	*Total cobalt found mg*	*% difference*
$[Co(NH_3)_5Cl]Cl_2$	A	100.2	100.4	+0.2
	A	100.2	100.2	0
	B	100.5	100.8	+0.3
	B	100.5	100.6	+0.1
	C	100.4	100.7	+0.3
	C	100.4	100.7	+0.3
	D	100.2	100.3	+0.1
	D	100.2	100.4	+0.2
J. M. sponge II	A	100.9	100.4	—0.5
(as sulphate)	A	100.9	100.5	—0.4
	B	100.1	99.5	—0.6
	B	100.1	99.6	—0.5
J. M. wire	A	100.2	100.6	+0.4
(as sulphate)	A	100.2	100.6	+0.4
	B	100.2	100.4	+0.2
	B	100.2	100.4	+0.2
$K_3[Co(CN)_6]$	B	76.9	77.0	+0.1
	B	76.9	77.0	+0.1
	C	72.3	72.5	+0.2
	C	72.3	72.4	+0.1
$CoSO_4$	D	100.6	101.1	+0.5
	D	100.6	101.2	+0.6

Co sponge II was not the same batch used in Series I.
$CoSO_4$ D was prepared from anhydrous $CoSO_4$ ignited at 530°.
For sponge and wire, A and B refer to different solutions made from the same sample.

A comparison of Series I and II indicates that in relation to the complexes, cobalt sponge I differs slightly in purity from sponge II. In relation to the sponge, the wire has a higher cobalt content. It is probable that in the process of manufacturing the wire from sponge, the oxide content is reduced.

The relatively high result obtained for the mixed sulphate would result if there were a deficiency in water of hydration as a result of drying, a potential source of error in all hydrated salts used for this purpose.

$CoSO_4$ gives erratic results, which suggests that slight decomposition occurs at the temperatures used and confirms previous doubts as to its value as a primary standard.

The complexes have many qualities that make them suitable for use as primary standards, *e.g.* absence of hydrated water and high molecular weight. In view of this and their mutual agreement and position relative to the other standards examined in the present work, it is recommended that they should be used as primary standards in cobalt analysis. The results indicate that their actual composition agrees closely with the theoretical composition. Of the three, the pentammine complex is the easiest to prepare and purify. It has been used for all further work in this series.

TABLE V

SUMMARY OF RESULTS

	Standard	*Mean relative error for phosphate method used %*
Series I	$[Co(NH_3)_5Cl]Cl_2$	+0.54
	$[Co(NH_3)_6]Cl_3$	+0.45
	$K_3[Co(CN)_6]$	+0.57
	Co sponge I	+0.20
	$CoSO_4 \cdot K_2SO_4 \cdot 6H_2O$	+0.92
	$CoSO_4$	+0.45 (but results erratic)
Series II	$[Co(NH_3)_5Cl]Cl_2$	+0.19
	$K_3[Co(CN)_6]$	+0.17
	Co sponge II	−0.50
	Co wire	+0.30
	$CoSO_4$	+0.55

TABLE VI

To indicate the amount of filtrate cobalt, two typical results are given in full.

Standard being examined	*Co taken mg*	*Phospate method used*	*Co found as $Co_2P_2O_7$ mg*	*Filtrate Co by N·R·S mg*	*Total Co mg*
$[Co(NH_3)_6]Cl_3$	100.1	I	100.1	0.4	100.5
$[Co(NH_3)_5Cl]Cl_2$	100.4	II	99.0	1.7	100.7

The cobalt sponge, although admirable, no doubt, for many purposes, cannot be recommended for use as a standard. The cobalt wire examined was evidently a very pure specimen. The only disadvantages in using it as a standard is that weighing errors would have the maximum effect.

It is not suggested that only the complexes recommended are suitable as cobalt primary standards. Probably many other compounds such as carbonatotetrammine cobaltic nitrate would give similar results. However, very few compounds other than those considered have been used for the purpose, and the standards mostly used have been those indicated as unsuitable in the present work. It is desirable that all papers on cobalt analysis should state clearly the standard used or the method used to standardise the stock solution, and in the latter case, for reasons given earlier, full details should be given.

SUMMARY

A number of primary standards for use in cobalt analysis have been compared under controlled conditions using the phosphate method of analysis. $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $K_3[Co(CN)_6]$ are recommended in preference to others which have hitherto been used for the purpose.

RÉSUMÉ

Les auteurs ont examiné plusieurs composés en vue de leur utilisation comme étalon pour l'analyse du cobalt. $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ et $K_3[Co(CN)_6]$ sont recommandés.

ZUSAMMENFASSUNG

Als Testsubstanzen für Kobaltbestimmungen werden folgende Verbindungen vorgeschlagen: $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ und $K_3[Co(CN)_6]$.

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RAPID ESTIMATIONS OF ZONE CONTENT IN PAPER CHROMATOGRAPHS

VI. R.Lf. METHOD

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In a previous paper the writer described an electro-static discharge method[1] whereby rapid approximate zone content estimations can be made. Since that was published he has carried out similar estimations by means of his rectified low-frequency apparatus described in this journal[2]. This alternative method has several advantages:

1. An ordinary micro-ammeter is employed in place of the delicate reflecting galvanometer used in the other method.

2. No "keys" are required[1].

3. As soon as a sample of solution has been drawn up into the conductimetric tube the micro-ammeter deflection *remains at a constant reading* until the tube is emptied

and the solution is returned to its original container, and the needle then returns to zero.

Preliminary procedure

The mode of proceeding is similar to that required for the "static discharge method". First a $N/500$ solution of the required solute is prepared and a graph is plotted "Solution concentration *vs.* μA". Fig. 1 is a sample graph.

Commencing with a carefully dispensed solution which in this case was an aqueous solution of nickel chloride, a series of dilutions were made by additions of two ml between each reading down to $N/3000$ and after that volumes of 10 ml were added till the graph was completed.

Approximate determination of zone content

Having located the zone or spot, that section of the chromatograph is excised and the content of the zone is dissolved in a measured volume of the solvent. It is best to commence with a small volume in case the spot is very small or is only a poor conductor. Should this solution prove to be too conductive the volume 'X' must be increased by a suitable amount which will bring the meter reading within the range of its scale.

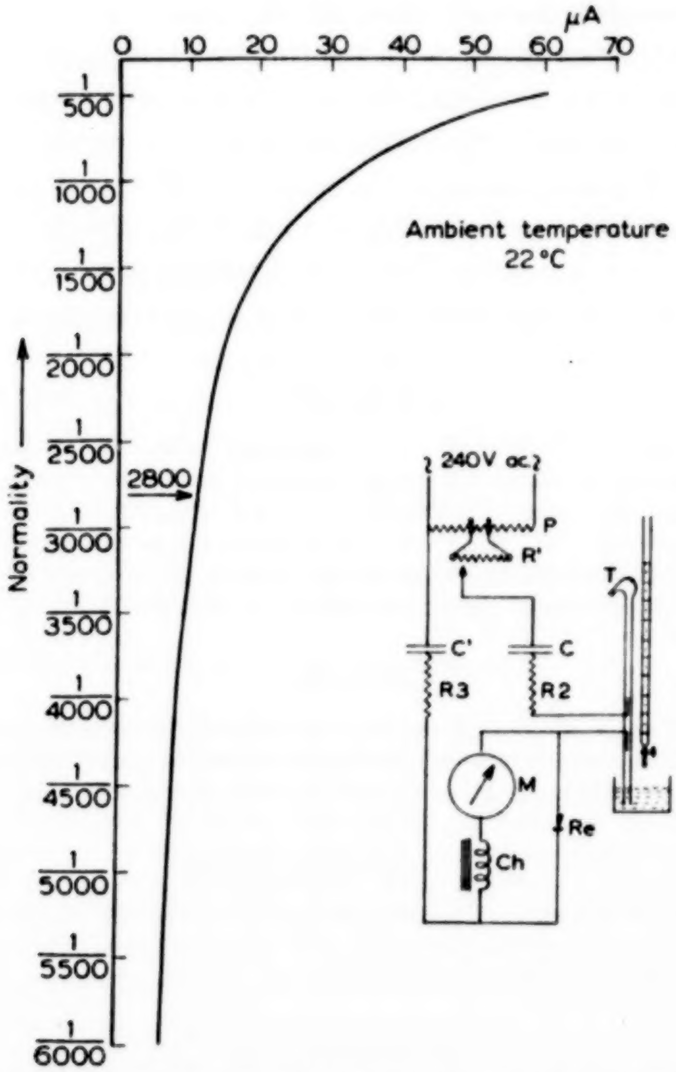

Fig. 1. This graph plotted on squared paper shows a series of nickel chloride concentrations plotted against current in μA. The arrow indicates the position of the sample spot on the graph. The inset on this figure shows the ac. R.I.f. circuit employed.

A sample of the solution is drawn up into the conductimetric tube T and the first reading is plotted. In the example which follows this reading was 60 μA. Fig. 1* gives a diagram of the electrical circuit.

Procedure

The approximate zone content is found by $N \cdot x/c$ when N = mol. wt. in g per l; c = concentration of solution and x = volume of the solvent in which the zone is dissolved.

Example

A reading of 10.1 μA was obtained for a solution made by dissolving a nickel chloride spot in 10 ml of distilled water 129.6/2800 × 10. Therefore the spot contained approximately 0.46 mg. The same circuit provides also a reliable method for dispensing and matching solution concentrations.

Comparison of the utility of the Electro-static discharge and the Rectified Low-frequency methods

The static discharge circuit is more sensitive towards the zero end of the scale and it undoubtedly provides the better method by which to estimate the relative purities of samples of water, also for the detection of an impurity, as for example, when it is required to ascertain the cleanliness of a conductimetric tube. Operation at near the zero end of the galvo.-scale is comfortably slow and precise readings are easily obtained. However as conductivity of the solution increases the speed of the galvo swing accelerates and it becomes more difficult to take readings.

When the R.Lf. circuit is employed there is no difficulty at all in taking readings, as the needle of the micro-ammeter remains stationary for as long as the conductimetric tube is full, however this method is less sensitive when near the zero end of its scale.

SUMMARY

The employment of BLAKE's "Rectified Low-frequency" circuit for plotting graphs for rapid determinations of the content of chromatograph zones is described. Comparison is made between this and his "Electro-static discharge" method. It is seen from graphs that either method may be used over the range required. The R.Lf. circuit presents several advantages for this work in general, but when the solute content is less than one part in 10.000 as is the case when samples of distilled water are to be compared the Static discharge method is by far the better.

RÉSUMÉ

L'appareil de BLAKE ("Rectified Low-frequency") est décrit en vue de son utilisation pour la détermination rapide des concentrations des zones chromatographiques. On compare avec la méthode de décharge électrostatique. Pour de très faibles concentrations, cette dernière donne de meilleurs résultats.

ZUSAMMENFASSUNG

Es wird die Anwendung von BLAKE's "Rectified Low-frequency" Apparat zur raschen Konzentrationsbestimmung in chromatographischen Zonen beschrieben und mit seiner "Electro-static Discharge" Methode vergleichen. Bei sehr kleinen Konzentrationen gibt die letztere Methode bessere Werte.

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* For constructional details of Fig. 1. see Ref. 1.

SPECTROPHOTOMETRIC STUDIES ON THE NATURE OF IRON COMPLEXES WITH PYRIDINE- AND QUINOLINE-CARBOXYLIC ACIDS

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SKRAUP[1] observed that pyridine- and quinoline-carboxylic acids, with a carboxyl group in the α-position to the heterocyclic nitrogen atom produce intense yellow or red colours with ferrous iron; methods for the determination of iron with quinaldinic[2,3], picolinic[4] and benzoquinaldinic[5] acids have been based on this reaction.

MAJUMDAR AND SEN[3-5] found that in solution the metal ion and the organic acid, in the absence of potassium cyanide, formed a 1 : 2 complex. However, SHINRA *et al.*[6] suggested the formation of a 1 : 3 complex between the metal and picolinic or quinaldinic acid, while RAY AND BANERJEE[7] found a ratio of 1 : 2 for quinaldinic acid and 1 : 3 for picolinic acid. These workers obtained dissociation constants for the complexes of the order of $3.63 \cdot 10^{-6}$ and $5.07 \cdot 10^{-12}$ respectively, whereas WENGER *et al.*[8] found a value of $2.6 \cdot 10^{-8}$ for ferrous quinaldinate, and MAJUMDAR AND SEN[4] a value of $4.23 \cdot 10^{-5}$ for ferrous picolinate.

These discrepancies necessitated a critical investigation of the composition and dissociation constants of the complexes formed in solution by ferrous ion with pyridine and quinoline carboxylic acids in the presence or absence of potassium cyanide.

EXPERIMENTAL

Apparatus and solutions

A Hilger Uvispek spectrophotometer was employed for optical density measurements at room temperature (25°) with 1-cm quartz cells. Corrections were made for any slight differences in the transmittancies of the cells.

A Cambridge pH meter was used for all pH determinations.

Iron solution: A standard solution was prepared by dissolving ferric nitrate, A.R., B.D.H., in twice distilled water. It was standardized and weaker solutions were prepared by dilution.

Reagent solution: α-Picolinic acid[13] (m.p. 130–132°), quinaldinic acid[14] (m.p. 155–157°) and quinolinic acid[15] (m.p. 192–194°) were prepared. A 1% solution of each was used.

Other solutions used were a 1.5 *M* (approx. 10%) solution of potassium cyanide, a 1% solution of hydroxylamine hydrochloride, sodium acetate–acetic acid and ammonium acetate–acetic buffers of pH 5.9.

Colour reactions and absorption maximum regions

The orange-yellow complex formed by ferrous ion with picolinic or quinolinic acid[12] either in presence of potassium cyanide (pH 9.0) or in presence of a large excess of the reagent (pH 5.9) showed maximum absorption at 440 mμ. The pink-red complex of iron and quinaldinic acid in the absence of potassium cyanide at pH 5.9 gave the absorption maximum at 480 mμ though the optical density remained constant up to 500 mμ; the complex formed in the presence of potassium cyanide had the maximum absorption at 515 mμ with no change in absorption values up to 520 mμ. In Fig. 1, curves Ia, Ib and Ic represent the optical density values in presence of potassium cyanide of the coloured complexes formed with 8 p.p.m. of iron; curves IIa, IIb and IIc present the values obtained at pH 5.9 in absence of potassium cyanide with 12 p.p.m. of iron.

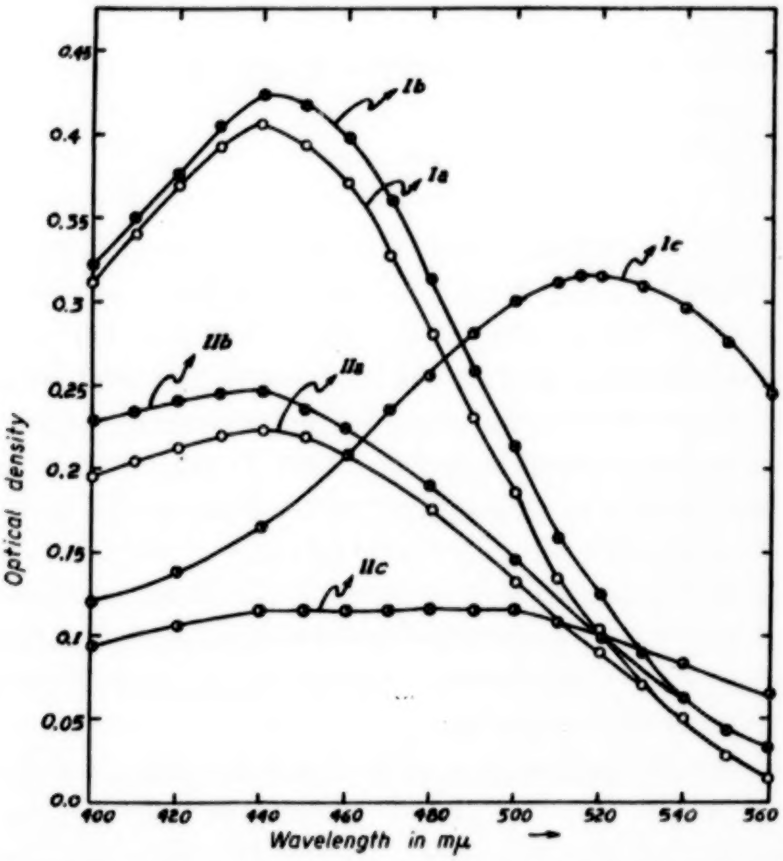

Fig. 1. Spectral transmittancy curves: Ia, IIa – picolinic acid complex; Ib, IIb – quinolinic acid complex; Ic, IIc – quinaldinic acid complex.

Composition of the complexes

The composition of the complexes in solution was determined by Job[9] and molar ratio[10] methods.

For Job's method, equimolar solutions of iron and reagent were taken in different quantities (total 10 ml) in 25-ml flasks. The iron solution was mixed with 1 ml of hydroxylamine hydrochloride, and the necessary amount of reagent, 1 ml of potassium cyanide and water to make up the volume were added. Curves A, B and C (Fig. 2) represent the picolinic, quinaldinic and quinolinic acid complex systems respectively.

In the absence of potassium cyanide, a large excess of reagent was required for maximum colour development. With equimolar solutions the reagent concentration was small and the optical density of the coloured complexes formed without cyanide was slightly higher at 420 mμ than at 440 mμ in the case of picolinic and quinolinic acids. The absorption maximum always occurred at 480 mμ with quinaldinic acid. The compositions of the picolinic and quinolinic acid complexes were determined both at 420 mμ and at 440 mμ and that of quinaldinic acid at 480 mμ by following the procedure given above except that 8 ml of the buffer pH 5.9 solution were added instead of 1 ml of the potassium cyanide solution. (Sodium acetate–acetic acid buffer was used in the picolinic and quinolinic acid systems while ammonium acetate–acetic acid buffer was more suitable for the quinaldinic acid complex; the former buffer formed a precipitate in the latter system.) Curves D, E and F (Fig. 2) represent respectively the picolinic, quinaldinic and quinolinic acid systems formed without cyanide. From the curves it can easily be inferred that in presence of potassium cyanide, the metal forms a 1 : 1 complex with these acids, whereas without cyanide the ratio is always 1 : 2.

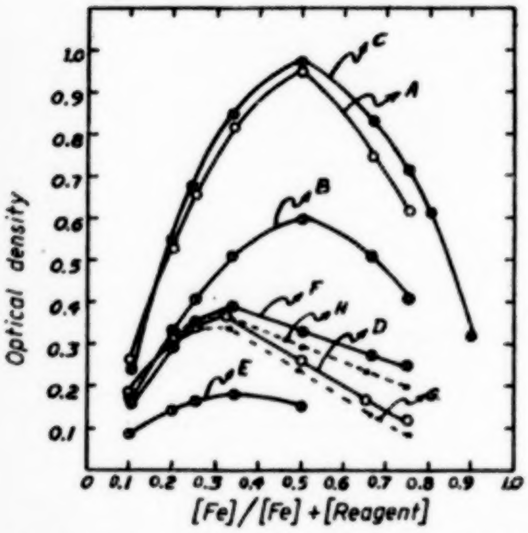

Fig. 2. Job's method of continuous variation: A – Fe = picolinic acid = $2.5 \cdot 10^{-3}$ M at 440 mμ; B – Fe = quinaldinic acid = $2.5 \cdot 10^{-3}$ M at 515 mμ; C – Fe = quinolinic acid = $2.66 \cdot 10^{-3}$ M at 440 mμ; D and F – Fe = picolinic and quinolinic acids respectively = $5 \cdot 10^{-3}$ M at 420 mμ; E – Fe = quinaldinic acid = $5 \cdot 10^{-3}$ M at 480 mμ; G and H – Fe = picolinic and quinolinic acids respectively = $5 \cdot 10^{-3}$ M at 440 mμ.

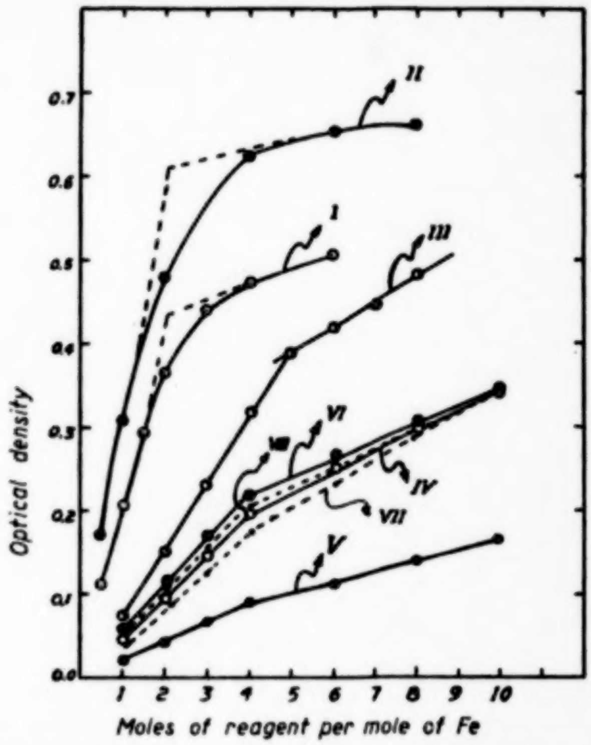

Fig. 3. Molar ratio method: I – 2 ml of $2.5 \cdot 10^{-3}$ M Fe and $2.5 \cdot 10^{-3}$ M picolinic acid at 440 mμ; II – 2 ml of $5 \cdot 10^{-3}$ M Fe and $5 \cdot 10^{-3}$ M quinaldinic acid at 515 mμ; III – 1 ml of $5.32 \cdot 10^{-3}$ M Fe and $1.064 \cdot 10^{-3}$ M quinolinic acid at 440 mμ; IV and VI – 2 ml of $5 \cdot 10^{-3}$ M Fe and $5 \cdot 10^{-3}$ M picolinic and quinolinic acids respectively at 420 mμ; V – 2 ml of $5 \cdot 10^{-3}$ M Fe and $5 \cdot 10^{-3}$ M quinaldinic acid at 480 mμ; VII and VIII – 2 ml of $5 \cdot 10^{-3}$ M Fe and $5 \cdot 10^{-3}$ M picolinic and quinolinic acids respectively at 440 mμ.

For the molar ratio method, the optical density values of the solutions were obtained by adding varying amounts of the organic acids and a fixed amount of potassium cyanide to a constant amount of iron; the values are shown in Fig. 3. The breaks in curves I, II and III indicate that for all the complexes the metal and the reagent were in a ratio of 1 : 1.

The data for the curves IV, V and VI (Fig. 3) were obtained by adding different amounts of the reagents ($5 \cdot 10^{-3}$ M) to 2 ml of an iron solution of the same molarity and by adjusting the pH to 5.9, without adding cyanide. The curves IV and VI show the absorption at 420 mμ and curve V that at 480 mμ. The breaks indicate a metal to reagent ratio of 1 : 2. Even when the measurements for the picolinic and quinolinic acid complexes were made at 440 mμ, after the addition of potassium nitrate to increase the ionic strength, the metal to reagent ratio of 1 : 2 remained unchanged. Curves G and H (Fig. 2) by Job's method, and VII and VIII (Fig. 3) by the molar ratio method, support this statement.

It is thus conclusively shown that in the absence of potassium cyanide, iron in solution is associated with pyridine and quinoline carboxylic acids in a ratio of 1 : 2 and that in presence of cyanide the ratio is 1 : 1. The formulae of the complexes may be suggested as:

Reagent	*with potassium cyanide*	*without potassium cyanide*
Quinolinic	$K_4[Fe(C_7H_3NO_4)(CN)_4]$	$Na_2[Fe(C_7H_3NO_4)_2(H_2O)_2]$
α-Picolinic acid	$K_3[Fe(C_6H_4NO_2)(CN)_4]$	$Fe(C_6H_4NO_2)_2(H_2O)_2$
Quinaldinic acid	$K_3[Fe(C_{10}H_6NO_2)(CN)_4]$	$Fe(C_{10}H_6NO_2)_2(H_2O)_2$

Instability constants of the complexes

The instability constant *K* of the complexes, formed in the presence or absence of potassium cyanide, was calculated by the following equations[11],

$$\alpha = \frac{Em - Es}{Em} \quad \text{and} \quad K = \frac{\alpha C(n\alpha C)^n}{C(1-\alpha)}$$

where α, *Em*, *Es*, *C* and *n* have their usual significances. The results are given in Table I.

TABLE I

Complex with	*Instability constant, K*	
	with potassium cyanide	*without potassium cyanide*
α-Picolinic acid	$2.51 \cdot 10^{-5}$	$1.53 \cdot 10^{-8}$
Quinaldinic acid	$7.51 \cdot 10^{-6}$	$2.02 \cdot 10^{-8}$
Quinolinic acid	$2.73 \cdot 10^{-5}$	$1.72 \cdot 10^{-9}$

MAJUMDAR AND SEN[4] found a higher value ($4.23 \cdot 10^{-5}$) for ferrous picolinate possibly because they used solutions of low pH. The instability constant found for ferrous-quinaldinate agrees fairly well with the values of WENGER *et al.*[8] ($2.6 \cdot 10^{-8}$). Increase of ionic strength by the addition of potassium nitrate had no effect on the final result.

SUMMARY

The compositions of the ferrous iron complexes with α-picolinic, quinaldinic and quinolinic acids have been reinvestigated. In presence of potassium cyanide, iron combines with these reagents in a ratio of 1 : 1; at pH 5.9, in absence of cyanide, the metal to reagent ratio is 1 : 2. The instability constants of the complexes are given.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique sur la composition des complexes ferreux des acides α-picolique, quinaldique et quinoléique.

ZUSAMMENFASSUNG

Es wird eine spektrophotometrische Untersuchung über die Zusammensetzung der Eisen(II)-Komplexe von α-Picolin-, Chinaldin- und Chinolinsäure beschrieben.

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THERMOLYSIS OF SULPHIDES PRECIPITATED BY SODIUM SULPHIDE

II. SULPHIDES OF SELENIUM, TELLURIUM, GOLD, PLATINUM, RUTHENIUM, LEAD, BISMUTH, CADMIUM, SILVER, PALLADIUM AND INDIUM

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The thermolysis of several sulphides precipitated by sodium sulphide has already been studied[1]. The present investigation deals with the thermolysis of the remaining sulphides. $Ir_2S_3 \cdot 10H_2O$ has been studied by Duval *et al.*[2].

EXPERIMENTAL

The reagents and methods for the preparation of the precipitates were as reported in earlier papers. The precipitates taken for thermolysis were in exactly the same condition as those used in the gravimetric determinations just before weighing.

A standard Stanton thermobalance was used. The rate of heating was 5.3 ± 0.2° per min. Palladium sulphide required a maximum temperature above 800°; to obtain automatically a linear rate of heating the high and low switches were preset at 3 and 1 respectively. The thermograms shown were obtained by plotting different points of the original graph on the X and Y axes.

Selenium disulphide

Oven-dried selenium disulphide[3] started to volatilize at 210° and had volatilized completely at 520°. (Fig. 1).

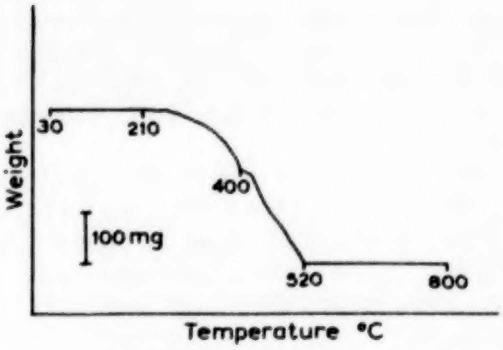

Fig. 1. Thermal decomposition curve of selenium sulphide (SeS_2) precipitated by sodium sulphide reagent.

Tellurium disulphide

Oven-dried tellurium disulphide[3] lost weight from 180° to 370°. From 370° to 410° the horizontal corresponded to metallic tellurium. From 410° to 620° a gain in weight showed the formation of TeO_2. The horizontal after 620° corresponded to TeO_2. (Fig. 2).

Tellurium trisulphide

The oven-dried precipitate[4] lost weight from 180° to 380°. From 380° to 430° the horizontal corresponded to metallic tellurium. From 430° the weight increased and TeO_2 was formed completely at 630°. The horizontal from 630° to 800° showed TeO_2. (Fig. 2).

Gold sulphide

Oven-dried gold sulphide[5] gave a horizontal up to 220°; it then started to lose weight and was completely converted to the metal at 280°. (Fig. 2).

Platinum sulphide

An air-dried sample of the pentahydrate[6] lost water and sulphur from 50° to 310°. From 310° the horizontal found corresponded to the metal. (Fig. 3).

The trihydrate[7] behaved in exactly the same way.

Ruthenium sulphide ($Ru_2S_3 \cdot 2H_2O$)

The air-dried precipitate[6] lost weight from 60° to 180°. The horizontal found at 180° to 240° did not correspond to the anhydrous form. From 240° to 340° there was a continuous gain in weight; the horizontal found from 340° to 410° did not correspond to any definite compound. After 410° the precipitate lost weight and was completely converted to the metal at 500°. (Fig. 3).

Lead sulphide

The air-dried precipitate[8] gave a horizontal up to 110°, after which it continuously gained weight. The gain became very small after 500°. (Fig. 4).

Bismuth sulphide

The oven-dried precipitate[8] gave a horizontal up to 160°; no other horizontal corresponded to any definite composition. (Fig. 4).

Cadmium sulphide

The oven-dried precipitate[8] lost 3–4% in weight from 50 to 140°, after which there was no further loss up to 300°. Above 300° it gained weight without any horizontal. (Fig. 4).

Silver sulphide

The air-dried precipitate[9] gave a near horizontal up to 570°; the gain in weight of about 1% may be due to impurities. From 570° to 710° the weight decreased and then increased continuously up to 800°. (Fig. 5).

Palladium sulphide ($PdS \cdot 2H_2O$)

The air-dried precipitate[6] lost weight from 50° to 420°. From 420° to 430° the weight increased and then decreased from 450° to 460°. From 460° to 800° it increased smoothly. Between 800° and 840° the horizontal found corresponded to PdO. From 840° to 890° the weight decreased and the metal was formed. (Fig. 5).

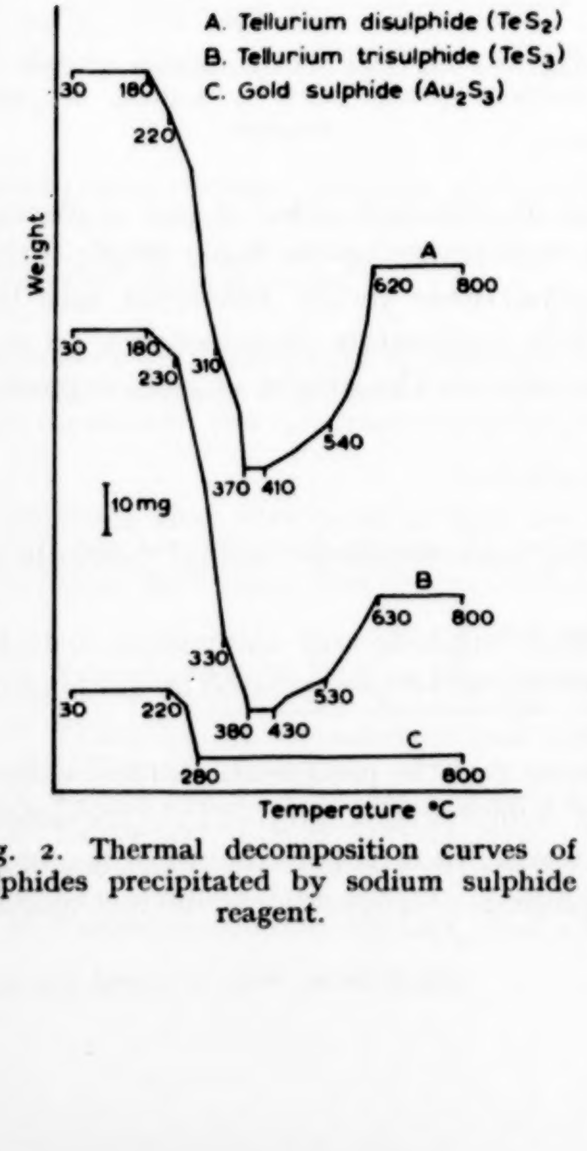

Fig. 2. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent.

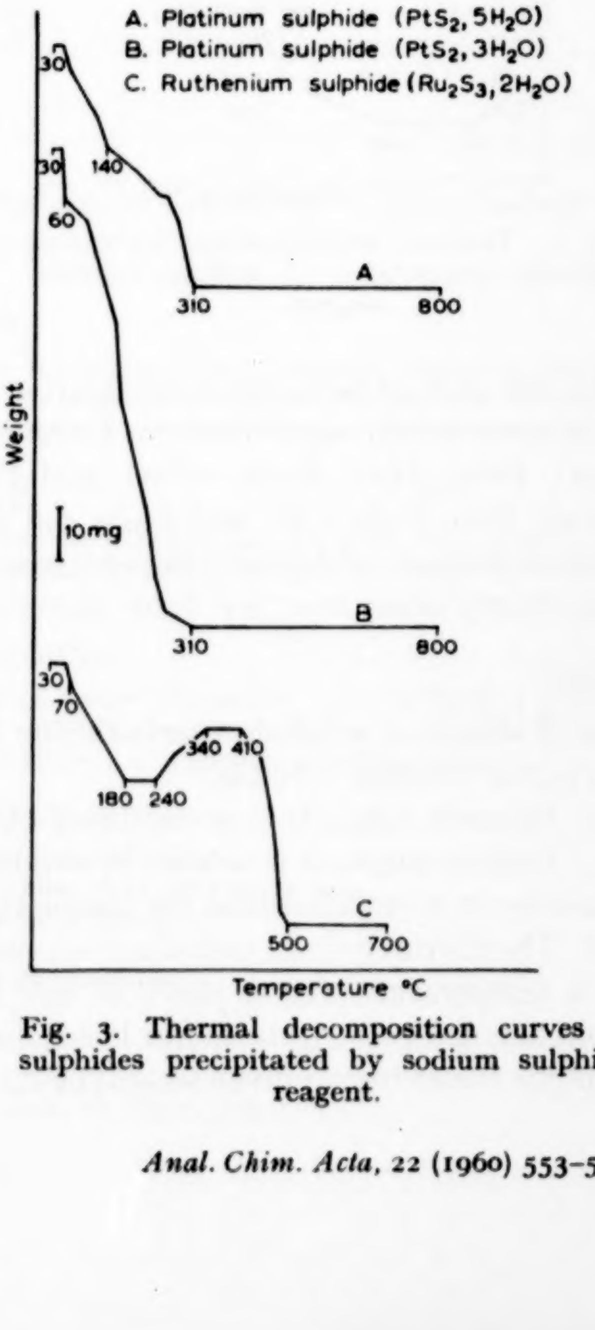

Fig. 3. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent.

Indium sulphide

The oven-dried precipitate[8] lost about 3% in weight from 50° to 100° after which it remained constant up to 340°. Above 340° the weight decreased continuously. (Fig. 5).

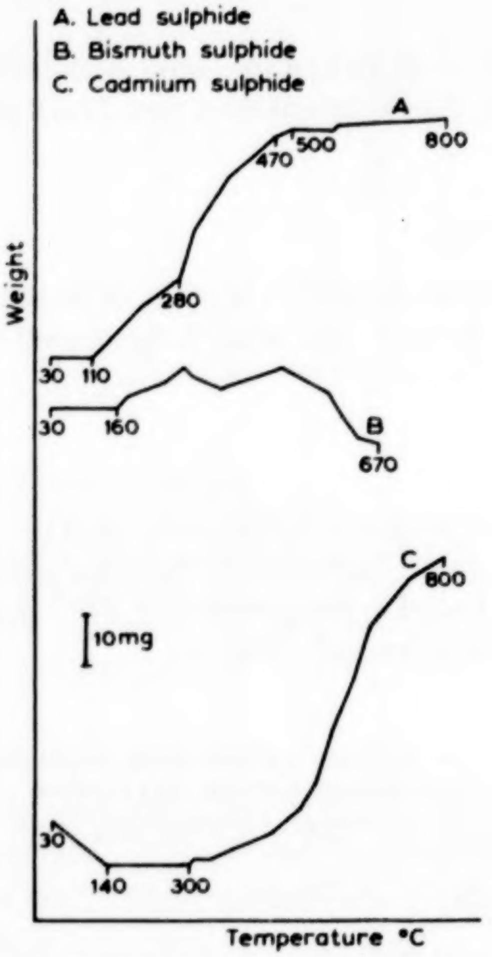

Fig. 4. Thermal decomposition curves of sulphides precipitated by sodium sulphide reagent.

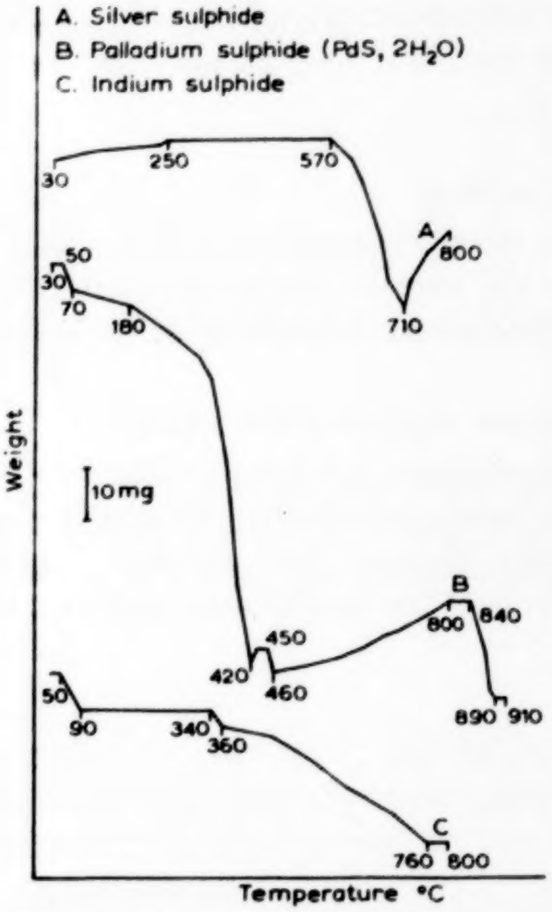

Fig. 5. Thermal decomposition curves of sulphide precipitated by sodium sulphide reagent.

In the case of SeS_2, the volatilization began at 210° and ended at 520°. TeS_2 and TeS_3 were finally converted to TeO_2 which was stable up to 800°. Au_2S_3, $PtS_2 \cdot 5H_2O$, PtS_2, $3H_2O$, $Ru_2S_3 \cdot 2H_2O$, and $PdS \cdot 2H_2O$ were finally converted into the metals. PbS, Bi_2S_3, CdS and In_2S_3 did not give horizontals corresponding to any definite formula at higher temperatures. The error in the weight of gold is greater than in any other case (see Table 1).

Notes:

a. Ruthenium sulphide spurts during heating and should be heated carefully in the partly covered crucible.

b. Bismuth sulphide is precipitated by sodium sulphide and ammonium acetate.

c. Indium sulphide is soluble in sodium sulphide and is precipitated by ammonium sulphide; it is included here for completeness.

d. The thermolysis of cadmium sulphide shows that the precipitate should be dried at a temperature above 140°. If the lower temperature, 105°–115°, previously recommended is used, the factor is not quite correct. In fact, the amount of cadmium sulphide found from a given weight of the sulphate is 3–4% higher than the theoreti-

TABLE I

TeS_2 taken (mg)	*Te calculated (mg) (370°–410°)*	*Te from graph (mg) (370°–410°)*	*TeO_2 calculated (mg) (620°–800°)*	*TeO_2 from graph (mg) (620°–800°)*
229	152	153	191	191
159	106	107	132	132
TeS_2 taken (mg)	*Te calculated (mg) (380°–430°)*	*Te from graph (mg) (380°–430°)*	*TeO_2 calculated (mg) (630°–800°)*	*TeO_2 from graph (mg) (630°–800°)*
175	100	101	125	123
176	100	101	125	119
	Au_2S_3 taken (mg)	*Au calculated (mg) (280°–800°)*	*Au from graph (mg) (280°–800°)*	
	104	84	91	
	96	77	85	
	Platinum sulphide taken (mg)	*Pt calculated (mg) (310°–800°)*	*Pt from graph (mg) (310°–800°)*	
$PtS_2 \cdot 5H_2O$	111	64	64	
$PtS_2 \cdot 3H_2O$	238	148	145	
$Ru_2S_3 \cdot 2H_2O$ taken (mg)	*Weight from graph (180°–240°)*	*Weight from graph (340°–410°)*	*Ru calculated (mg) (500°–700°)*	*Ru from graph (mg) (500°–700°)*
130	107	117	78	79
103	87	95	62	60
$PdS \cdot 2H_2O$ taken (mg)	*PdO calculated (mg) (800°–840°)*	*PdO from graph (mg) (800°–840°)*	*Pd calculated (mg) (890°–910°)*	*Pd from graph (mg) (890°–910°)*
246	172	180	150	160
254	178	184	155	163

cal value. It is therefore necessary to use the conversion factor 0.75191 instead of 0.77840 to calculate the amount of cadmium metal.

SUMMARY

Thermolysis of selenium, tellurium, gold, platinum, ruthenium, lead, bismuth, cadmium, silver, palladium or indium sulphide precipitated by sodium sulphide has been studied. The methods used for drying and weighing these sulphides are reliable, except in the case of cadmium where an empirical factor is needed.

RÉSUMÉ

Une étude a été effectuée sur la thermolyse de sulfures précipités par le sulfure de sodium. Les conditions de séchage et de pesée des sulfures de sélénium, de tellure, d'or, de platine et de ruthénium conviennent très bien à leur dosage gravimétrique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das thermolytische Verhalten von Sulfiden. Es wird gezeigt, dass die üblichen Methoden der Trocknung und Wägung der Sulfiden von Selen, Tellur, Gold, Platin, Ruthenium, Blei, Wismut, Silber, Palladium und Indium zuverlässig sind.

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OXIDATIONS WITH POTASSIUM PERMANGANATE IN PRESENCE OF FLUORIDE

II. POTENTIOMETRIC TITRATION OF MERCURY(I) AND THE REDOX POTENTIAL OF THE Mn^{+7}/Mn^{+3} SYSTEM

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The direct titration of mercury(I) in sulphuric acid medium in the presence of fluoride[1] provides a useful determination; and back-titration of permanganate with mercurous solution can be applied for the determination of manganese in steels containing chromium and vanadium[2]. However, the visual procedure is only successful in the titration of dilute solutions; otherwise the pink colour of trivalent manganese interferes seriously. RAO *et al.*[3] have also studied the oxidation of mercury(I) in hydrochloric acid medium with permanganate but they preferred iodine monochloride as catalyst.

We have now studied the potentiometric titration of mercury(I) with permanganate and the reverse titration in order to discover whether the method is satisfactory for more concentrated solutions.

EXPERIMENTAL

Potentiometric equipment

The titration device was similar to that previously described[4]; a potassium nitrate salt bridge was used.

Preparation and standardization of solutions

The potassium permanganate solutions were prepared by a method similar to that of STAMM[5] and standardized by sodium oxalate[6]. The solutions used were 0.1958 *N*, 0.0482 *N* and 0.0241 *N*, based on a valency change of 5. However, for the present calculations the normalities should be multiplied by 0.8.

Mercurous solutions were prepared as before[1] and standardized by titration with potassium permanganate. The solutions prepared were 0.1024 *N*, 0.0512 *N* and 0.0256 *N*.

Other solutions: 9 *N* sulphuric acid, 2% NaF, and 0.25 *N* $CuSO_4$.

RESULTS AND DISCUSSION

I. Titration of mercury(I) with potassium permanganate

The reaction of mercurous solution with potassium permanganate proceeded more or less rapidly at the beginning of the titration but as the end-point was approached the reaction became rather sluggish needing about 5 min to attain equilibrium. A systematic study of the different factors affecting the accuracy of results was made.

TABLE I

Titration of 10 ml 0.1024 *N* $Hg_2(NO_3)_2$ (205.5 mg Hg_2^{+2}) with 0.1958 *N* $KMnO_4$ using varying quantities of 9 *N* H_2SO_4 in presence of 50 ml 2% NaF.

Volume of H_2SO_4 *ml*	*Volume of $KMnO_4$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* *%*	*Max. inflection mV/0.02 ml*
1.0	5.89	6.54	9.94	80
2.5	6.54	6.54	0.00	192
5.0	6.52	6.54	0.31	156
10.0	6.54	6.54	0.00	146
15.0	6.63	6.54	1.38	163
20.0	6.70	6.54	2.45	111

The effect of acidity

The results shown in Table I indicate that the concentration of sulphuric acid could vary from 0.36 *N* to 1.29 *N*, without greatly affecting the values. However, at concentrations of 1.8 *N* and 2.25 *N* larger errors were obtained. The end-points appeared later than the equivalence points, which was ascribed to a slight production of quadrivalent manganese (a faint brown turbidity).

TABLE II

Titration of 5 ml 0.0512 *N* $Hg_2(NO_3)_2$ with 0.0481 *N* $KMnO_4$ in presence of 50 ml 2% NaF

Volume of 9 N H_2SO_4 *ml*	*Time of exposure to atmospheric oxygen before titration* *min*	*Volume of 9 N H_2SO_4* *ml*	*Volume of $KMnO_4$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* *%*
—	5	5	6.67	6.65	0.30
—	30	5	6.67	6.65	0.30
1	5	4	6.65	6.65	0.00
1	20	4	6.68	6.65	0.45
1	60	4	6.67	6.65	0.30

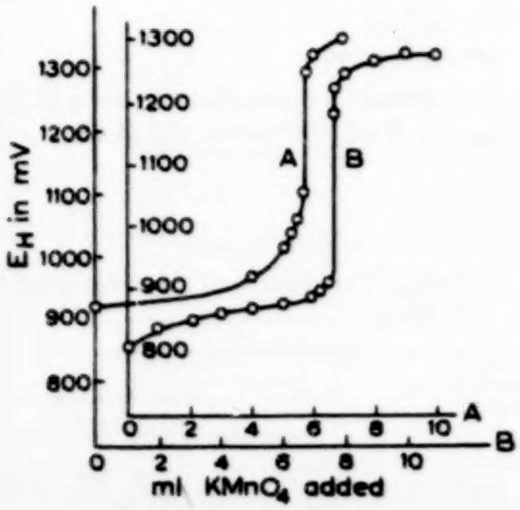

Fig. 1. Titration of 10 ml 0.1024 *N* $Hg_2(NO_3)_2$ in 50 ml 2% NaF and different volumes of 9 *N* H_2SO_4 with 0.1958 *N* $KMnO_4$. A. 20 ml H_2SO_4, B. 2.5 ml H_2SO_4.

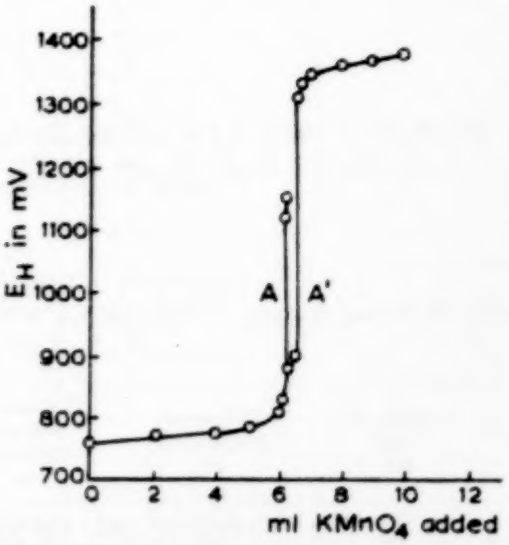

Fig. 2. Titration of 10 ml 0.0512 *N* $Hg_2(NO_3)_2$ in 50 ml 2% NaF. A. in presence of 1 ml 9 *N* H_2SO_4, A'. after end-point of A, 4 ml 5 *N* H_2SO_4 were added and the titration continued.

When the sulphuric acid concentration was less than 0.15 N, the end-points appeared much too early. This error cannot be due to atmospheric oxidation of mercury(I) in alkaline solutions, for mercurous fluoride mixtures could be left in contact with the atmosphere for one hour while stirring without the titre being affected. However when the solution was brought to the correct acidity and titrated further with permanganate, a drop in potential was observed and when the titration was completed the second end-point was found to agree with the theoretical value (*cf.* Fig. 2 and Table II). The titration curves obtained at different sulphuric acid concentrations (Fig. 1) indicate that the inflection at the end-point decreases with rise of acidity.

The effect of sodium fluoride

The results shown in Table III and Fig. 3 indicate that the fluoride concentration could vary from 0.07 M to 0.42 M, the amount of sulphuric acid remaining constant without appreciable errors. At the lower fluoride concentration, the reaction was slow near the end-point taking about 8 min to attain equilibrium. At higher fluoride concentrations the reaction was more rapid. There was no exact relation between the fluoride concentration and the size of the inflection at the end-point.

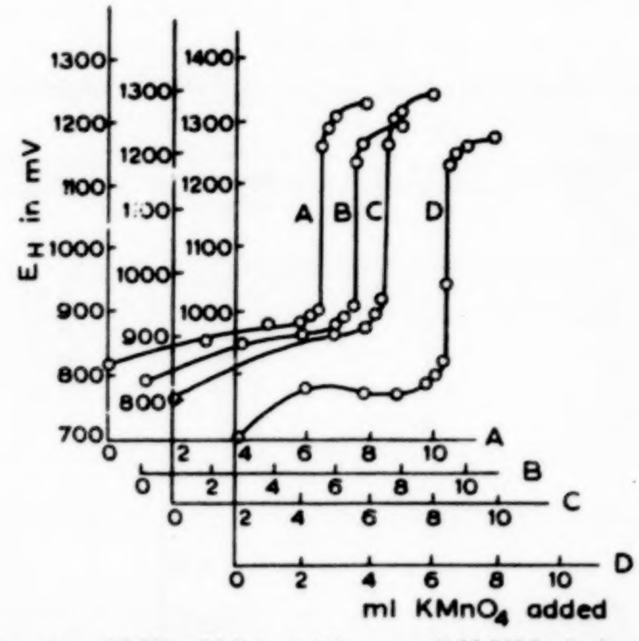

Fig. 3. Titration of 10 ml 0.1024 N $Hg_2(NO_3)_2$ with 0.1958 N $KMnO_4$ in presence of 5 ml 9 N H_2SO_4 A. 75 ml 2% NaF, B. 100 ml 2% NaF, C. 50 ml 1% NaF, D. 50 ml 2% NaF.

TABLE III

Titration of 10 ml 0.1024 N $Hg_2(NO_3)_2$ with 0.1958 N $KMnO_4$ in presence of varying quantities of 2% NaF and 5 ml 9 N H_2SO_4

Volume of NaF ml	*Volume of H_2O added ml*	*Volume of $KMnO_4$ consumed ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
10	40	6.53	6.54	0.15	80
50	—	6.52	6.54	0.31	156
70	—	6.54	6.54	0.00	136
100	—	6.52	6.54	0.31	92

The effect of mercurous concentration

The results given in Table IV indicate that when the amounts of fluoride and sulphuric acid remained constant, the method could be used to determine from 25 to 616 mg of mercury. The potentiometric method was therefore satisfactory for higher concentrations of mercury(I) than the visual method. The inflection at the end-point decreased with increasing mercury concentration (Fig. 4). It is noteworthy that mercury gave a turbidity with sulphuric acid which became more evident with increasing mercurous concentration.

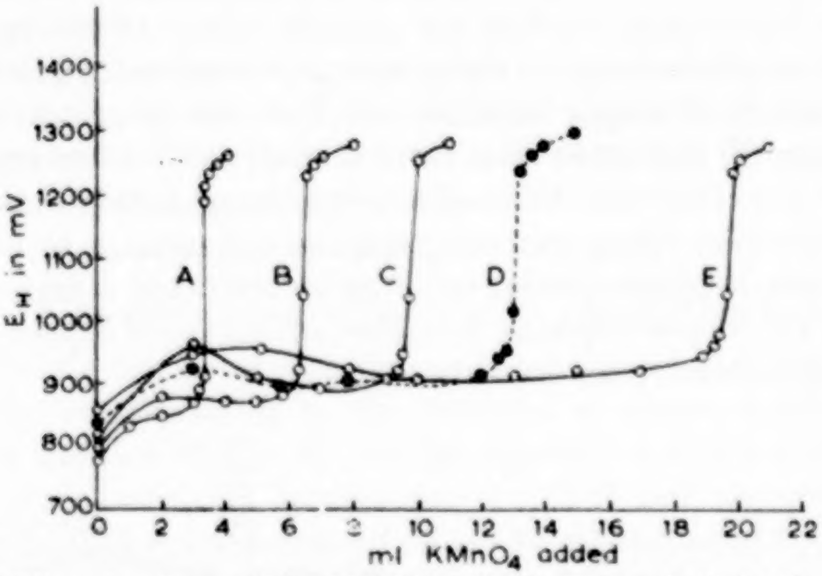

Fig. 4. Titration of different volumes of 0.1024 N $Hg_2(NO_3)_2$ in 50 ml 2% NaF and 5 ml 9 N H_2SO_4 with 0.1958 N $KMnO_4$. A. 5 ml, B. 10 ml, C. 15 ml, D. 20 ml, E. 30 ml.

TABLE IV

Titration of $Hg_2(NO_3)_2$ with $KMnO_4$ in presence of 5 ml 9 N H_2SO_4 and 50 ml 2% NaF

Mercury (I) titrated ml	*Vol. of $KMnO_4$ consumed ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
Titration of 0.01024 N $Hg_2(NO_3)_2$ with 0.1958 N $KMnO_4$				
10	6.52 [a]	6.54	0.31	156
10	6.50 [b]	6.54	0.62	106
10	6.49 [c]	6.54	0.93	103
15	9.82	9.81	0.1	90
30	19.62	19.62	0.00	84
Titration of 0.0512 N $Hg_2(NO_3)_2$ with 0.04814 N $KMnO_4$				
5	6.68	6.65	0.45	126
Titration of 0.0256 N $Hg_2(NO_3)_2$ with 0.02407 N $KMnO_4$				
10	13.21	13.3	0.68	128

[a] at 25°, [b] at 40°, [c] at 55°

The effect of temperature

Table IV indicates that accurate results could be obtained by carrying out titrations at ordinary temperature (25°) under the optimum conditions *i.e.* 1 N sulphuric acid and 0.4 M sodium fluoride. The error increased to 0.93 % at 55°. The end-point appeared before the theoretical value probably owing to the decomposition of some permanganate at higher temperatures or to the increased ability of mercury(I) to reduce manganese(VII) to the manganous state. However, a rise of temperature increased the reaction rate enormously and it is preferable to carry out the titration at 40°.

The effect of copper ion on the reaction

The results obtained under varying conditions of acidity, fluoride and copper(II) concentrations were the same as in the absence of copper. Copper(II) was especially important when more concentrated solutions were titrated, for it enhanced the reaction and its blue colour masked the pinkish colour of the manganic fluoride complex, so that as much as 273.3 mg of mercury could be determined by a visual titration. The amount of copper sulphate which should be present increased as the amount of mercury(I) increased. The ratio of copper(II) to mercury(I) should lie between 1:1 and 3:1. However, because some permanganate is consumed before the appearance of the violet colour characterising the end-point, a blank must be determined. The amount of permanganate required for the blank is higher, the higher the concentration of the copper sulphate. A further advantage of copper(II) is that in its presence the titration curves are smoother (*cf.* Fig. 5).

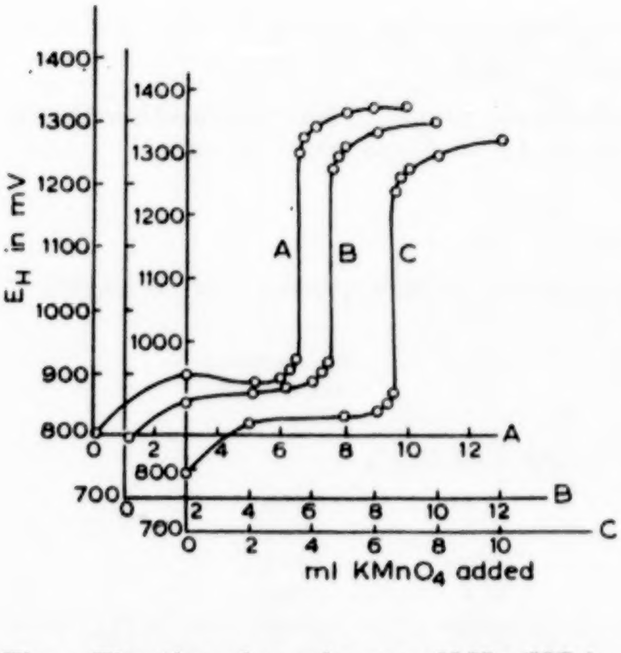

Fig. 5. Titration of 10 ml 0.1024 N $Hg_2(NO_3)_2$ in 50 ml 2% NaF and 9 N H_2SO_4 with 0.1958 N $KMnO_4$. A. in absence of $CuSO_4$, B. in presence of 5 ml 0.25 M $CuSO_4$, C. in presence of 10 ml 0.25 M $CuSO_4$.

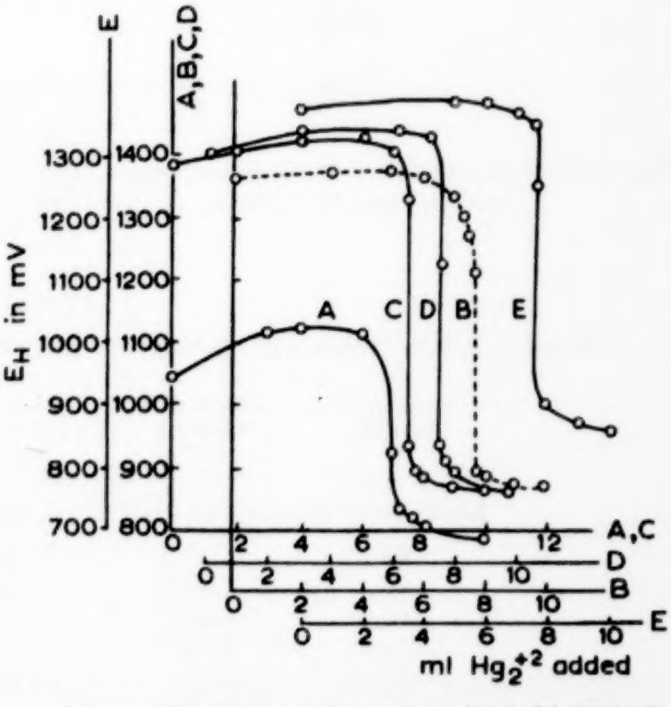

Fig. 6. Titration of 5 ml 0.1958 N $KMnO_4$ in 50 ml 2% NaF and different volumes of 9 N H_2SO_4 with 0.1024 N $Hg_2(NO_3)_2$. A. in absence of H_2SO_4, B. 4 ml H_2SO_4, C. 5 ml H_2SO_4, D. 10 ml H_2SO_4, E. 5 ml H_2SO_4 and 5 ml 0.25 M $CuSO_4$.

II. Titration of potassium permanganate with mercury(I)

The effect of acidity

The titration curves of permanganate with mercurous solution at different acidities are shown in Fig. 6. The curves are characterised by sharp inflections which do not vary in regular manner with acidity.

In the absence of sulphuric acid, the end-point was attained earlier than the theoretical value (Table V); this was due to the formation of a brown turbidity of manganese dioxide. When the solutions were 0.24 *N*, 0.38 *N* and 0.61 *N* in sulphuric acid and contained 50 ml of 2% fluoride, the end-points coincided with the theoretical values. In 0.75 and 1.38 *N* sulphuric acid, the end-points appeared too early because of partial decomposition of potassium permanganate which increased with the rise of acidity.

Note

That early end-points were not due to partial production of manganese dioxide was confirmed as follows:

5 ml of 0.1958 *N* permanganate were titrated with 0.1024 *N* mercurous nitrate in the presence of 0.75 *N* sulphuric acid; the end-point appeared at 7.57 ml. The volume of mercurous nitrate added was then completed to 10 ml and the excess was titrated with permanganate, when 1.59 ml were used.

The total volume of $KMnO_4$ = 6.59 ml
the total volume of Hg_2^{+2} = 10 ml
theoretically 10 ml of Hg_2^{+2} = 6.54 ml $KMnO_4$

If, however, the early end-point was due to the production of manganese dioxide, then the end-point corresponding to the titration of excess mercury(I) should be attained after the addition of 1.54 ml; for the dioxide would react with the mercury added and give manganese(III). In presence of 1.38 *N* acid the volume of permanganate consumed by the excess mercury(I) was 1.68 ml instead of 1.59 in the presence of 0.75 *N* acid. Accordingly the end-point appeared later by an amount equivalent to the permanganate decomposed.

TABLE V

Titration of 5 ml 0.1958 *N* $KMnO_4$ (10.75 mg Mn) with 0.1024 *N* $Hg_2(NO_3)_2$ using varying quantities of 9 *N* H_2SO_4 in presence of 50 ml 2% NaF

Volume of 9 N H_2SO_4 ml	*Volume of $Hg_2(NO_3)_2$ ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
—	7.0	7.65	8.5	194
1	7.56	7.65	1.18	234
1.5	7.63	7.65	0.25	213
4	7.62	7.65	0.39	208
5	7.55	7.65	1.31	255
5	7.65	7.65	0.00	257 *
10	7.4	7.65	3.27	199
10	7.59	7.65	0.79	393 *

* in presence of 5 ml 0.25 *M* $CuSO_4$

The errors obtained at high acidities decreased in the presence of copper(II) because the reaction was then enhanced and the tendency to autodecomposition was minimized.

Effect of sodium fluoride

The curves in Fig. 7 and the data in Table VI show that good results were obtained at concentrations of sodium fluoride of 0.12 *M* to 0.42 *M*. However, with 0.05 *M*–0.02 *M* fluoride and an acidity of 0.23 *N* sulphuric acid, the end-points appeared very late owing to the tendency of potassium permanganate to yield bivalent manganese in the presence of less sodium fluoride. This is confirmed by carrying out the following experiment:

5 ml of 0.1958 *N* permanganate were mixed with 10 ml of 2% sodium fluoride, 40 ml of water and 2.5 ml of 9 *N* sulphuric acid. The solution was titrated with 0.1024 *N* mercurous solution and the end-point appeared after 9.35 ml had been added. The volume of mercury(I) solution was completed to 10 ml and the excess was then titrated with permanganate. The end-point appeared after the addition of 0.5 ml.

The total volume of mercurous solution = 10 ml
the total volume of $KMnO_4$ = 5.5 ml
volume of $KMnO_4 \equiv$ to mercurous = 6.54 ml

The smallness of the volume of permanganate consumed compared to the mercurous present indicates the formation of manganese(II), since the latter is not oxidised by permanganate in acid medium. The solution under these conditions is quite clear and colourless due to the absence of manganese(III).

Increasing the fluoride concentration decreases the magnitude of the inflection at the end-point (Fig. 7).

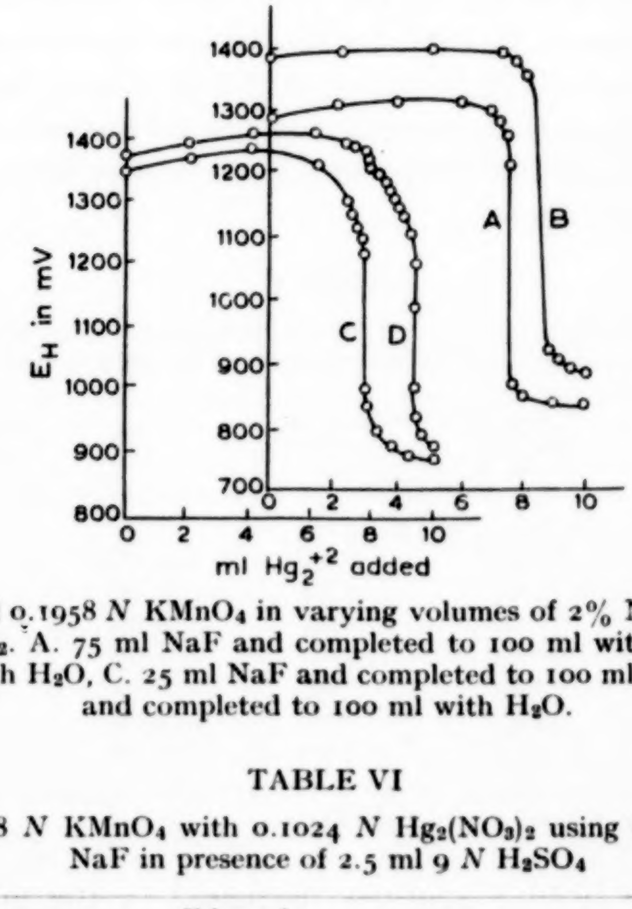

Fig. 7. Titration of 5 ml 0.1958 *N* $KMnO_4$ in varying volumes of 2% NaF and 2.5 ml 9 *N* H_2SO_4 with 0.1024 *N* $Hg_2(NO_3)_2$. A. 75 ml NaF and completed to 100 ml with H_2O, B. 5 ml NaF and completed to 100 ml with H_2O, C. 25 ml NaF and completed to 100 ml with H_2O, D. 10 ml NaF and completed to 100 ml with H_2O.

TABLE VI

Titration of 5 ml 0.1958 *N* $KMnO_4$ with 0.1024 *N* $Hg_2(NO_3)_2$ using varying quantities of 2% NaF in presence of 2.5 ml 9 *N* H_2SO_4

Volume of NaF used ml	*Volume of H_2O added ml*	*Volume of $Hg_2(NO_3)_2$ consumed ml*	*Theoretical end-point ml*	*Error %*	*Max. inflection mV/0.02 ml*
75	17.5	7.61	7.65	0.52	216
50	—	7.64	7.65	0.13	138
25	67.5	7.69	7.65	0.52	155
10	82.5	9.35 colourless	7.65	22.22	89

Effect of permanganate concentration

Amounts of manganese ranging from 1.3 mg up to 32 mg could be determined with reasonable accuracy (Table VII). The inflections at the end-points (Fig. 8) were sharp and generally increased as the permanganate concentration increased.

TABLE VII

Titration of $KMnO_4$ with $Hg_2(NO_3)_2$ in presence of 2.5 ml 9 *N* H_2SO_4 and 50 ml 2% NaF

$KMnO_4$ *ml*	*Titrated Mn* *mg*	*Vol. of $Hg_2(NO_3)_2$ consumed* *ml*	*Theoretical end-point* *ml*	*Error* %	*Max. inflection* *mV*
Titration of 0.1958 N $KMnO_4$ with 0.1024 N $Hg_2(NO_3)_2$					
5 [a]	10.755	7.64	7.65	0.13	138
5 [b]	10.755	7.65	7.65	0.00	199
5 [c]	10.755	7.58	7.65	0.93	210
15	32.265	23.04	22.95	0.39	171
Titration of 0.04814 N $KMnO_4$ with 0.0512 N $Hg_2(NO_3)_2$					
10	5.293	7.56	7.52	0.53	162
Titration of 0.02407 N $KMnO_4$ with 0.0256 N $Hg_2(NO_3)_2$					
10	2.647	7.55	7.52	0.4	238

[a] at 25°; [b] at 40°; [c] at 55°.

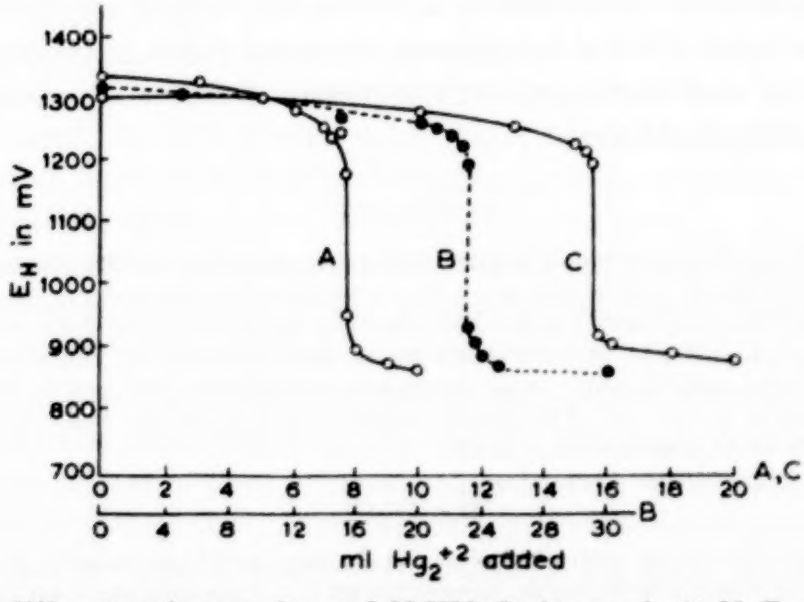

Fig. 8. Titration of different volumes of 0.1958 *N* $KMnO_4$ in 50 ml 2% NaF and 2.5 ml 9 *N* H_2SO_4 by 0.1024 *N* $Hg_2(NO_3)_2$. A. 5 ml $KMnO_4$, B. 15 ml $KMnO_4$, C. 10 ml $KMnO_4$.

Effect of temperature

The results in Table VII show that a rise of temperature caused some decomposition of potassium permanganate; early end-points were obtained at 55°. Accurate results, as in the reverse titration, could be obtained at ordinary temperatures or at 40°.

The redox potentials of the Mn^{+7}/Mn^{+3} system

The redox potentials of the Mn^{+7}/Mn^{+2} and the Mn^{+7}/Mn^{+4} system have been measured or calculated from free energy data. However, a value for the Mn^{+7}/Mn^{+3} couple is not known. This value can be found from the titration curves of perman-

TABLE VIII

Normality of H_2SO_4	—	0.24	0.39	0.75	1.38
Formal potential of the Mn^{+7}/Mn^{+3} system (V)	1.120	1.220	1.310	1.360	1.420
Normality of NaF	0.02	0.05	0.12	0.36	0.42
Formal potential of the Mn^{+7}/Mn^{+3} system (V)	1.400	1.410	1.390	1.310	1.310
Normality of H_2SO_4	—	0.15	0.36	0.69	2.25
Formal potential of the Hg^{+2}/Hg_2^{+2} system (V)	0.73	0.77	0.860	0.870	0.93
Normality of NaF	0.07	0.18	0.37	0.42	
Formal potential of the Hg^{+2}/Hg_2^{+2} system (V)	0.980	0.880	0.860	0.850	

ganate with the mercurous solution in the presence of fluoride. Trivalent manganese is kept in solution; the potential set by a bright platinum electrode when 50% of the permanganate has been reduced represents the formal redox potential of the system. The values shown in Table VIII indicate that the redox potential of the Mn^{+7}/Mn^{+3} increases with rise of acidity and decreases with increase of fluoride concentration.

From the titration curves of mercurous solutions with potassium permanganate, the formal redox potential of the mercuric/mercurous couple can be evaluated. From the data shown in Table VIII it is apparent that the redox potential again increases with rise of acidity and decreases with increase of fluoride concentration. (These points will be investigated later).

SUMMARY

Mercury(I) can be titrated potentiometrically with permanganate in the presence of fluoride and sulphuric acid. The optimum conditions are 2.5–10 ml of 9 *N* acid and 10–100 ml of 2% sodium fluoride at a temperature of 25–40°. Larger amounts can be determined than in the visual method, although copper (II) is a suitable indicator screen in the titration of fairly large amounts. The reverse titration is also satisfactory; the optimum conditions are 1.5–4 ml of 9 *N* acid and 25–75 ml of 2% fluoride at 25–40°. The formal redox potential of the Mn^{+7}/Mn^{+3} couple is 1.4 V, in presence of 1.38 *N* H_2SO_4 and 0.12 *N* NaF.

RÉSUMÉ

Les auteurs proposent un titrage potentiométrique du mercure(I) au moyen de permanganate, en présence de fluorure et d'acide sulfurique. Inversément le permanganate a pu être titré aussi, avec succès, par une solution de mercure(I).

ZUSAMMENFASSUNG

Zur Bestimmung von Quecksilber(I) wird die potentiometrisch Titration mit Permanganat in Gegenwart von Fluorid und Schwefelsäure empfohlen. Umgekehrt lässt sich auch Permanganat mit Quecksilber(I) nach dieser Methode bestimmen.

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THE RAPID ANALYSIS OF SILICA IN REFRACTORIES AND MINERALS

AN IMPROVED METHOD OF SAMPLE PREPARATION

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INTRODUCTION

Rapid semi-micro photometric procedures for the determination of silica in refractories and minerals are well established. A simple method for the dissolution of siliceous materials prior to colorimetric estimation of silica is required.

The following methods of sample preparation have been reported. RILEY[1] fused the sample with sodium hydroxide in a silver crucible at 800 – 850°. SHAPIRO AND BRANNOCK[2] and ARCHER *et al.*[3], fused the sample with sodium hydroxide in a nickel crucible and leached the fusion overnight with water. The range of materials decomposed was limited and the time required for water-leaching excessive. The contamination by nickel and silver salts was undesirable and the crucibles were appreciably attacked and difficult to clean.

HARPHAM[4] recommended sodium peroxide fusions for certain minerals resistant to decomposition by other methods. Finely powdered materials (240-B.S. sieve) were completely decomposed when sintered for 7 min at 480° ± 10° in an electric muffle furnace. Either acidification or 50–100 ml of cold water, completely and rapidly dissolved the cake. The sintering was effected in platinum crucibles without any attack on the platinum, or in iron or nickel vessels with insignificant attack on the metal. It was also reported that many substances were decomposed at 200° with even less attack on the vessels. Extremely resistant minerals were decomposed by fusion with sodium peroxide at the lowest possible temperature using iron, nickel or platinum crucibles. PETRETIE[5] recommended the use of zirconium crucibles because they were extremely resistant to sodium peroxide fusions. Sodium peroxide treatment was considered to be most satisfactory because a wide range of materials were decomposed and water extraction was rapid.

Procedures for the estimation of silicon are described in the literature. These methods are based on the measurement of the yellow colour of silicomolybdic acid or on the blue colour of reduced silicomolybdic acid. KNUDSON, JUDAY AND MELOCHE[6] showed that in sulphuric acid medium, maximum colour development of silicomolybdate occurred at a pH of 1.6 – 2.0. The silicomolybdate formation was shown to be complete within 5 min and phosphate was the main interfering ion. KAHLER[7] used sodium sulphite as a reducing agent for silicomolybdate. LINDSAY AND BIELENBERG[8] used 1-amino-2-naphthol-4-sulphonic acid together with sulphite as reducing agent.

BUNTING[9] stated that the blue reduction colour was stable for several days when tartaric acid was used to prevent iron and phosphate interference and 1-amino-2-naphthol-4-sulphonic acid together with sulphite was used as the reducing agent.

EXPERIMENTAL AND DISCUSSION

A wide range of materials such as coal ash, slags, clays, ores, and refractories were readily decomposed by sintering with sodium peroxide in a platinum crucible. When sintering with sodium peroxide the average platinum loss was 0.5 mg, compared with 1–2 mg for a normal sodium carbonate fusion. The crucible was easily cleaned and the sintered mixture dissolved readily in water.

The concentration of sulphuric acid was controlled in order to obtain the maximum colour development and highest stability of the molybdenum blue reduction compound. The blue colour was stable for at least two days.

It was found that undecomposed peroxide interfered in the determination of silicon. The interference when using 0.075 mg silicon and 6.5 ml of 0.5% v/v sulphuric acid per 100 ml of assay is shown in Table I.

TABLE I

INTERFERENCE OF PEROXIDE

mg Na_2O_2	0.0	0.2	0.4	0.6	0.8	1.0	4.0	8.0	16.0[a]
Absorbance	0.572	0.573	0.574	0.574	0.573	0.574	0.536	0.434	0.281

[a] 16 mg of Na_2O_2 corresponds to 1.5 g of undecomposed peroxide in the original sample.

The peroxide interference appeared to be caused by the formation of a complex with ammonium molybdate. This interference could not be eliminated by increased ammonium molybdate addition. The peroxide interference was eliminated by the addition of potassium permanganate to the warm solution and the subsequent removal of the excess with dropwise additions of 1 volume hydrogen peroxide. The interference study shows that 1 mg of sodium peroxide can be tolerated, and in the suggested procedure one drop excess of hydrogen peroxide is equivalent to only 0.035 mg of sodium peroxide.

Aliquots taken from this preparation are also suitable for the determination of Al_2O_3, TiO_2 and Fe_2O_3 using the procedures of ARCHER *et al.*[3]

APPARATUS AND REAGENTS

Apparatus

Muffle furnace capable of maintaining a temperature of 500° ± 5°. *Polyethylene* ware should be used wherever possible. *Volumetric flasks*[10] should be reserved for this work only and treated as described to prevent silicon contamination. Clean overnight in chromic–sulphuric acid, rinse, and then fill overnight with 1 : 1 sulphuric–nitric acid which will render them insoluble. Rinse with distilled water. When not in use the flasks should be left filled with distilled water.

Reagents

Sodium peroxide, powdered AnalaR; 25% v/v sulphuric acid A.R.; 5% v/v sulphuric acid A.R.; 3.6% w/v potassium permanganate A.R. solution; 0.3% w/v hydrogen peroxide A.R. (1 volume); 1.5% w/v ammonium molybdate solution, dissolve 15.0 g of ammonium molybdate A.R. in 250 ml of water, add 200 ml of 5% sulphuric acid and dilute to 1000 ml with water; 8% w/v tartaric acid A.R. solution; reducing solution, dissolve 0.70 g of sodium sulphite A.R. in 20 ml of water, add 0.15 g of 1-amino-2-naphthol-4-sulphonic acid and stir until dissolved, dissolve 9.0 g of sodium metabisulphite A.R. in 180 ml of water and mix both solutions. Fresh reducer should be prepared each week.

RECOMMENDED PROCEDURE

Weigh 50 mg of finely ground sample (240 B.S. sieve) into a platinum crucible and mix with 1.0 g of powdered sodium peroxide using a platinum wire. Cover the mixture with a layer of 0.5 g of sodium peroxide and place in a muffle furnace at 500° and sinter for ten minutes. The temperature should not be allowed to exceed 500° because of accelerating attack on the platinum by molten sodium peroxide at higher temperatures.

Allow the crucible to cool, cover with a lid and half-fill with water. After the reaction has ceased and the crucible is cool, add 5.0 ml of 25% sulphuric acid. Add the contents of the crucible to a 200-ml plastic bottle containing 25.0 ml of 5% sulphuric acid and 15 ml of water. Leach the crucible with 15.0 ml of hot 5% sulphuric acid, scrub with a rubber policeman, and add the washings to the bottle.

Warm the bottle to 90° on a water bath and add 3.6% potassium permanganate solution dropwise until the solution is pink. Excess peroxide will be destroyed. Just decolourize the solution with the dropwise addition of 1 volume hydrogen peroxide solution. Cool and dilute to 1 litre. Store in a polyethylene bottle.

Transfer 2 × 10-ml aliquots to 100-ml volumetric flasks. A calibration series may be prepared by adding standard silicon solution to 10-ml aliquots of a blank which has been carried through the procedure.

Add 50 ml of water to standards, assays and blanks.

Assays

Add 5 ml of 1.5% ammonium molybdate solution, swirling during the addition. Allow to stand 10 min. Add 5 ml of 8% tartaric acid solution, mix and add 2.0 ml of reducing solution immediately. Mix and dilute to volume at once. Allow to stand 1 h for colour development.

Blanks

Add 5 ml of 8% tartaric acid, mix. Add 2.0 ml of reducing solution and mix. Add 5 ml of 1.5% ammonium molybdate solution, mix, dilute to volume and allow to stand 1 h.

Read the absorption at a wavelength of 813 mμ using a 10-ml aliquot and a 2-cm cell, samples containing 8–34% silicon obey Beer's law.

ACKNOWLEDGEMENT

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SUMMARY

A method of dissolution of siliceous material has been proposed, together with a method for the subsequent colorimetric estimation of silica as the molybdenum blue reduction compound. The finely ground samples are sintered at 500° with powdered sodium peroxide in platinum crucibles, the mixture extracted with water, and acidified. Excess peroxide is removed by oxidation with potassium permanganate. Silica is determined by reduction of yellow silicomolybdic acid with 1-amino-2-naphthol-4-sulphonic acid to the blue reduction compound. Phosphates and iron are masked with tartaric acid. The sample solution may also be used for the colorimetric determination of alumina, ferric oxide, and titania.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage de la silice dans des substances réfractaires et dans des minerais. L'attaque se fait par fusion au peroxyde de sodium; la silice est finalement dosée colorimétriquement, après réduction de l'acide molybdique en bleu de molybdène, au moyen de l'acide amino-1-naphthol-2-sulfonique-4.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur raschen Bestimmung von Silizium in Mineralien und keramischen Massen. Nach Aufschluss der Substanz durch Erhitzen mit Natriumperoxyd auf 500° im Platintiegel wird das Silizium kolorimetrisch bestimmt.

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THE POLAROGRAPHIC DETERMINATION OF HEXAVALENT URANIUM IN THE PRESENCE OF EXCESS FERRIC IRON

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Furman and Haight[1] have reported that uranyl ions give a wave at —0.5 V (*vs.* S.C.E.) in 0.01 M sodium fluoride and at —1.10 V in 1.0 M sodium fluoride. They also state that while ferric ions give a wave at —0.58 V in 0.01 M sodium fluoride, no wave due to iron is found when using the stronger supporting electrolyte.

West, Dean and Breda[2] have shown that sodium fluoride forms a complex with ferric iron which is so stable that the reduction potential is shifted to values more negative than the discharge potential of the sodium ions in the supporting electrolyte. Their observation is supported by Verdier *et al.*[3,4] and by recent work in these laboratories[5]. On the other hand various workers[6–10] have reported waves due to the reduction of ferric ions in fluoride media. Unfortunately, in most cases, the exact experimental conditions are not stated, and it is therefore difficult to compare the results of the various authors. As is shown later, pH, for example, has a large effect on the reduction of uranyl ions, and it is therefore a pity that much published work is rendered of little value to others by the lack of essential details. A review of published work has recently been compiled by one of the authors[5].

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This investigation was undertaken in order to determine whether the use of sodium fluoride as a supporting electrolyte would enable the rapid, quantitative estimation of hexavalent uranium in the presence of excess iron, with the aim of extension to the analysis of the "pregnant liquors" of the uranium mining industry, where uranyl ions must be determined in the presence of an approximately 200 fold excess of iron.

EXPERIMENTAL

Reagents

All reagents were tested to determine their polarographic purity. The sodium fluoride used was found to contain a small amount of lead (0.002%) which was not removed as the wave due to this impurity was only observed at high sensitivities; (20 mm/μA or higher, waveheight 0.02 μA) and, moreover, did not interfere with the determination of uranium.

In all cases, the uranium solutions were prepared by dilution of an exactly $1 \cdot 10^{-2}$ *M* solution of uranyl nitrate, standardised by the gravimetric procedure of precipitation as ammonium diuranate and ignition to U_3O_8.

Apparatus

All curves were recorded using a Cambridge pen-recording polarograph. The cells used were of the Cambridge 2-ml type, carrying an S.C.E., separated from the solution by means of an agar bridge, as a reference electrode.

pH measurements were made with a Beckman model H-2 meter with a Beckman glass electrode as indicator and an S.C.E. as reference.

Procedure

Polarograms were recorded at 25.0 ± 0.05°.

Oxygen was removed from the test solution by bubbling nitrogen for 10 min before recording. The capillary used had a mean drop-time of 3.64 sec/drop at zero applied potential and an *m* value of 0.001854 g/sec. 0.004% gelatin was used as a maximum suppressor.

Unless otherwise stated, the pH of the test solutions was 6.5 or greater, and the supporting electrolyte was 0.75 *M* sodium fluoride. To obtain these conditions solutions of iron and uranium of pH between 2.5 and 3.0 were diluted ten times with 0.8333 *M* sodium fluoride. If the original pH is below the limit stated above, the pH after addition of the fluoride solution is less than 6.5.

The reduction of uranyl ions alone in sodium fluoride

Although FURMAN AND HAIGHT[1] report only one wave for uranyl ions in 0.01 and 1.0 *M* sodium fluoride, it was found that, provided the pH of the test solution was 6.5 or greater, uranyl ions in 0.1, 0.25, 0.5 and 0.75 *M* sodium fluoride gave rise to two waves before the discharge potential of sodium ions. The waves tend to coalesce and the diffusion current plateau of the first wave ($E_{\frac{1}{2}}$ close to —0.65 V) is hardly developed. The second wave ($E_{\frac{1}{2}}$ close to —0.95 V), which is approximately twice the height of the first, has a well defined diffusion current plateau. These waves both correspond to an irreversible reduction process at the dropping mercury electrode, and the voltage span covering the two waves is —0.5 to —1.2 V. The half-wave potential of the first wave becomes slightly less negative with decreasing uranyl ion concentration, particularly below a concentration of 10^{-4} M, whereas that of the second wave remains constant. In all cases, and unlike ferric iron waves at low fluoride concentrations[5], the combined height of the two waves was time independent, remaining constant for periods of 12 hours.

As it is not possible to measure accurately the start of the second wave, any quantitative method for determination of uranyl ions must be based on the measurement of the sum of the diffusion currents of both waves. All wave-heights reported are therefore measured at —1.4 V and are the combined wave-heights of the two uranyl waves.

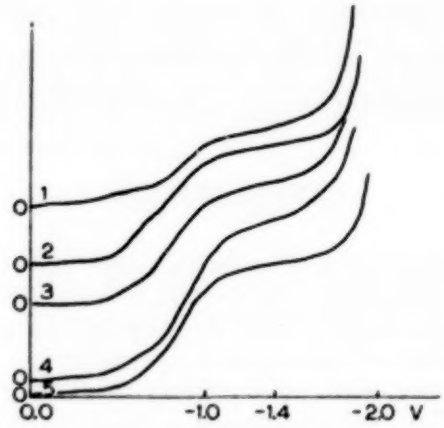

Fig. 1. Typical UO_2^{+2} curves. Curve 1. 10^{-4} M UO_2^{+2} in 0.75 M NaF, Sens. 1/10, Curve 2. 10^{-3} M UO_2^{+2} in 0.25 M NaF, Sens. 1/50, Curve 3. 10^{-3} M UO_2^{+2} in 0.75 M NaF, Sens. 1/50, Curve 4. $6 \cdot 10^{-4}$ M UO_2^{+2} in 0.75 M NaF, Sens. 1/20, Curve 5. $5 \cdot 10^{-3}$ M UO_2^{+2} in 0.75 M NaF, Sens. 1/200.

The behaviour of various concentrations of uranyl ions in 0.1, 0.25, 0.5 and 0.75 M sodium fluoride was studied. In all cases the pH of the test solution was greater than 6.5 and the measured wave-height decreased regularly with decreasing uranyl ion concentration between $5 \cdot 10^{-3} M$ and 10^{-5} M. The optimum range was found to be 10^{-4} to 10^{-3} M over which lineality existed. Concentrations of uranyl ion below $5 \cdot 10^{-5}$ M gave wave heights of less than 0.1 μA which were not considered analytically useful.

Typical polarograms are shown in Fig. 1, while Fig. 2 shows the relation between

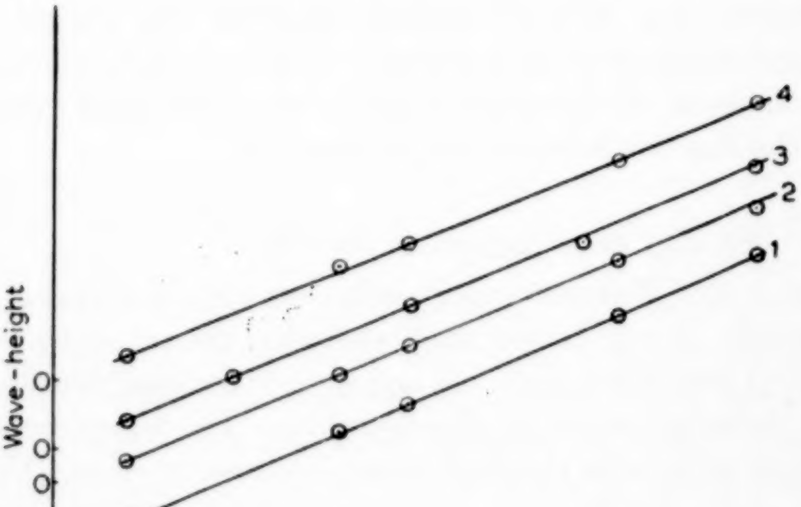

Fig. 2. Variation of wave-height with uranyl ion concentration. The zero wave-height of each curve is marked on the ordinate. Curve 1. 0.10 M NaF; 2. 0.25 M NaF; 3. 0.50 M NaF; 4. 0.75 M NaF.

wave-height and concentration of uranyl ion in the range 10^{-4} to 10^{-3} *M* for the various concentrations of supporting electrolyte used.

Effect of pH

Polarograms of 10^{-3} *M* uranyl nitrate in 0.5 and 0.75 *M* sodium fluoride, with various amounts of added hydrochloric acid, were recorded to observe the effect of pH on the curves. An effective buffering action was observed in this pH variation and was pronounced below a pH value of 5, as would be expected from the formation of the weak undissociated acid, hydrogen fluoride. The uranyl waves were found to be pH independent only when the pH of the test solution was 6.5 or higher. Since the reduction of hexavalent uranium involves hydrogen ions, it would be expected that any lowering of the pH would cause marked changes in the uranyl waves. From typical curves shown in Fig. 3, the great influence of pH on (*a*) the number of waves formed, (*b*) the half-wave potentials of these waves, and (*c*) the wave-heights for a given concentration of uranyl ion, may be seen. Although the wave-heights are greater, the adverse effects of acid solutions of sodium fluoride on the glass of the dropping mercury electrode, and the necessity for very accurate control of pH when this less than 6.5, made it desirable to work in neutral solution. All subsequent curves were thus recorded on solutions of pH in the range 6.5 to 7.8.

Since the large increase in wave-height of solutions having pH between 6.5 and 6.0 was also observed in uranyl acetate solutions acidified with hydrochloric acid, it does not seem that this increase in wave-height can be due to the well known effect[11] of nitrate ions on uranium waves.

Complexing of iron(III) by sodium fluoride

Recent studies in these laboratories[5] have shown that the use of 0.45 *M* sodium fluoride as a supporting electrolyte removes waves due to ferric iron up to a concentration of $2 \cdot 10^{-3}$ *M*. It was also shown that the efficient removal of these waves depended mainly on a high fluoride to ferric ion ratio. It was, therefore, decided to investigate the use of 0.75 *M* sodium fluoride as a supporting electrolyte, since weaker concentrations would not only prove less effective in complexing ferric ions, but would also have a less pronounced neutralising effect on acid solutions.

Efficient complexing of ferric ions by sodium fluoride does not occur unless the pH of the iron solution is between 2 and 3 before addition of the fluoride[4,5]. The amount of ferric ion which can be complexed by a particular sodium fluoride solution is thus limited by the pH of that solution (and therefore by the ionic concentration of the solution) as well as by the ratio of fluoride to ferric ions.

Using 0.75 *M* sodium fluoride as a supporting electrolyte it was found that waves due to ferric iron were not present up to a concentration of $5 \cdot 10^{-2}$ *M*.

Determination of uranium in the presence of excess ferric iron

Polarograms of 10^{-4} *M* uranyl nitrate and various concentrations of ferric iron in 0.75 *M* sodium fluoride were recorded. Table I shows the results obtained for the determination of uranium in these samples. In this series no acid was added to the solutions, so that it can be seen that simple polarography of uranyl and ferric ion mixtures in 0.75 M sodium fluoride allows the determination or uranium in the presence of up to a 400 times excess of ferric iron.

The precipitate of the complex fluoroferrate which forms on adding fluoride ions to ferric ions need not be filtered off before recording the polarogram as it has been shown[5] not to affect the result.

TABLE I

DETERMINATION OF UO_2^{+2} IN PRESENCE OF Fe^{+3}

Conc. UO_2^{+2} taken (M)	*Conc. Fe^{+3} (M)*	*Conc. UO_2^{+2} found (M)*	*Remarks*
$1 \cdot 10^{-4}$	—	$1 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$1 \cdot 10^{-2}$	$1.03 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$2 \cdot 10^{-2}$	$0.98 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$3 \cdot 10^{-2}$	$0.98 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$	$1.02 \cdot 10^{-4}$	
$1 \cdot 10^{-4}$	$5 \cdot 10^{-2}$	$1.14 \cdot 10^{-4}$	pH of test solution 6.3
$1 \cdot 10^{-4}$	$6 \cdot 10^{-2}$	$1.18 \cdot 10^{-4}$	pH of test solution 6.2
$1 \cdot 10^{-4}$	$7 \cdot 10^{-2}$	$1.64 \cdot 10^{-4}$	pH of test solution 6.1

Determination of uranium in the presence of acid and excess ferric iron

Since efficient complexing of ferric ions occurs between pH 2.0 and 3.0, any excess hydrogen ion present in the samples must necessarily be removed before addition of the supporting electrolyte. In order that the pH of all test solutions need not be strictly controlled to a constant value, this pH range must be narrowed to 2.5 to 3.0 in the procedure used. Under these conditions, addition of the sodium fluoride not only complexes the iron but also gives a final pH of 6.5 or greater.

Attempts at pH correction, by addition of hydroxyl ions at various stages in the preparation of the test solution, and by the use of buffer solutions, were not satisfactory. It was found that the elimination of pH effects, in samples containing added acid, was most conveniently achieved by evaporation of the solution to dryness before addition of the sodium fluoride supporting electrolyte. If the acidity is not due to either nitric or hydrochloric acid, it is recommended that the elements be precipitated as hydroxides, washed with water and then dissolved in the minimum amount of 20% nitric acid before evaporation to dryness. Baking on a hot plate of surface temperature about 140° for 2–4 min when dry, not only ensures complete volatilisation of any acid, but also removes some of the iron by decomposition of ferric nitrate to the insoluble oxide. Decomposition of the uranyl salt does not occur in this short time. Longer baking, however, results in some loss of uranyl ion by decomposition and a subsequent decrease in the height of the uranyl wave. Table II shows results obtained for various mixtures. The standard deviation of the method is 2.0%.

Interferences

Apart from the presence of molybdenum and vanadium, the effect of which has already been reported[1], the effect of the presence of Ti^{+3}, Mn^{+2}, Cu^{+2} and Pb^{+2} was studied. Fig. 4 shows polarograms of uranyl mixtures containing these ions.

TABLE II

DETERMINATION OF UO_2^{+2} IN PRESENCE OF EXCESS Fe^{+3} AND H^+

Conc. of UO_2^{+2} taken (M)	*In presence of*	*Conc. of UO_2^{+2} found (M)*	*Diff. %*
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$ *M* Fe^{+3} 2 *N* HCl	$0.975 \cdot 10^{-4}$	—2.5
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$ *M* Fe^{+3} 4 *N* H_2SO_4	$0.981 \cdot 10^{-4}$	—1.9
$1 \cdot 10^{-4}$	$4 \cdot 10^{-2}$ *M* Fe^{+3} 1 *N* HNO_3	$0.985 \cdot 10^{-4}$	—1.5
[a]$1 \cdot 10^{-3}$	$4 \cdot 10^{-1}$ *M* Fe^{+3} 2 *N* HCl	$0.982 \cdot 10^{-3}$	—1.8

[a] Solutions diluted ten times before evaporation to dryness.

Only titanium ($E_{\frac{1}{2}}$ —1.22 V) gives a wave within the voltage span of the uranium waves. The half-wave potential of Mn^{+2} (—1.54 V) is sufficiently negative to enable the tolerance of at least a 400 times excess in the presence of 10^{-4} *M* uranyl ion. Cupric ions are reduced at approximately —0.3 V so that their presence provides no difficulty unless they occur in excess. Lead should be previously largely removed as the sulphate if a precipitate of lead fluoride is to be avoided on addition of the supporting electrolyte. This is probably unimportant if the concentration of lead is of the order of 10^{-3} *M*, since the small reduction in concentration of the supporting electrolyte has been shown to make no difference to the wave-height of the uranyl wave, and since the lead fluoride may be removed from the test solution by filtration.

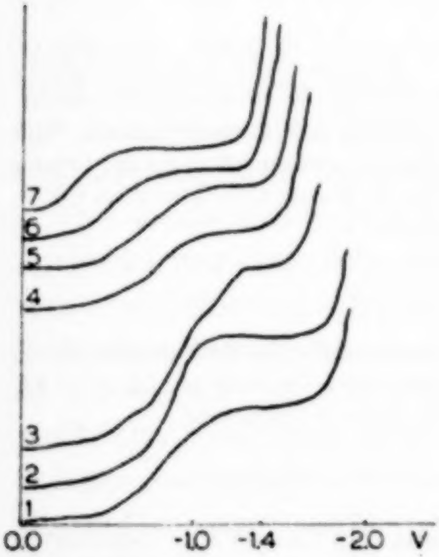

Fig. 3. Effect of pH on UO_2^{+2} curves: All curves on 10^{-3} *M* UO_2^{+2} in 0.5 *M* NaF; pH varied using HCl. Curves 1 – 3, Sens. 1/50; 4 – 7, Sens. 1/100. Curves 1 – 7 pH's of resp. 7.5, 6.4, 5.1, 4.3, 3.5, 2.3 and 1.4.

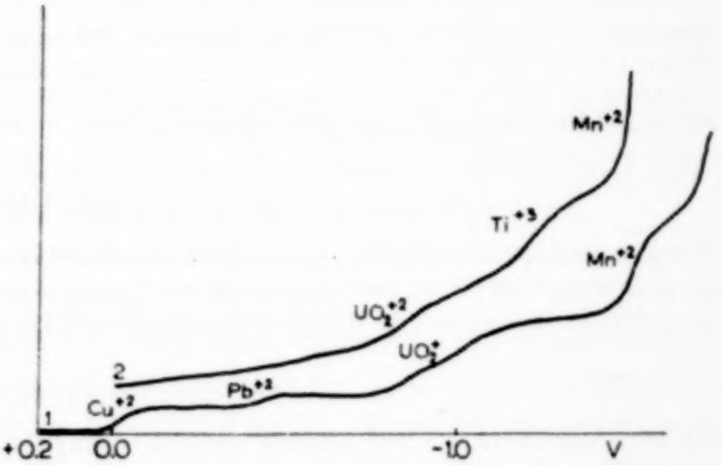

Fig. 4. 1. Polarogram of 10^{-4} *M* UO_2^{+2} in 0.75 *M* NaF in the presence of $5 \cdot 10^{-4}$ *M* Ti^{+3} and 10^{-3} *M* Mn^{+2}. Sensitivity 1/20. 2. Polarogram of a mixture of 10^{-3} *M* UO_2^{+2}, 10^{-3} *M* Cu^{+2}, 10^{-3} *M* Mn^{+2}, 10^{-3} *M* Pb^{+2} made up in 0.75 *M* NaF and filtered before recording. Sensitivity 1/100.

CONCLUSIONS

1. The rapid polarographic determination of hexavalent uranium, within the concentration range 10^{-3} to 10^{-4} M, and in the presence of up to 400 times excess of ferric iron and even larger amounts of free acid, is possible using 0.75 M sodium fluoride as a supporting electrolyte.

2. The presence of Cu^{+2}, Pb^{+2}, Mn^{+2} does not interfere with the procedure if they occur in amounts stated above. The presence of Ti^{+3}, or other interfering elements, would, however, necessitate prior separation, thus robbing the method of its simplicity and rapidity.

3. When using a dropping mercury electrode it is best to work in neutral fluoride solution (pH 6.5 or greater).

4. The standard deviation of the method is 2.0% so that determinations can be made with 95% confidence to an accuracy of 4.0%.

5. The method should prove applicable to the determination of uranyl ions in the "pregnant liquors" of the uranium mining industry. An investigation into this possibility is being undertaken and it is hoped to publish results shortly.

ACKNOWLEDGEMENTS

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SUMMARY

It is shown that concentrations of uranyl ions varying from 10^{-4} M to 10^{-3} M may be rapidly determined polarographically, to an accuracy of 4% (95% confidence), in the presence of concentrations of ferric iron up to four hundred times in excess of the uranyl ion concentration. The determination is insensitive to the concentration of the 0.75 M sodium fluoride used as a supporting electrolyte, and to time; but is not valid if the pH of the test solution is below 6.5. The ions Cu^{+2}, Pb^{+2} and Mn^{+2} are shown not to interfere, while Ti^{+3} must be removed.

RÉSUMÉ

Les auteurs ont examiné et mis au point une méthode de dosage polarographique de l'uranium(VI) en présence d'un excès de fer(III). On peut ainsi doser des teneurs en ions UO_2^{+2} de 10^{-3} à 10^{-4} M, en présence de fer(III) en très fortes concentrations, jusqu'à 400 fois celle de l'uranyle.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur polarographischen Bestimmung von Uran(VI) in Gegenwart eines Überschusses an Eisen(III), der das 400 fache der vorhandenen Menge Uran betragen kann. Der Einfluss von Fremdionen wird erwähnt.

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CONTROLLED POTENTIAL COULOMETRIC DETERMINATION OF TIN

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Although tin has been determined several times by controlled potential gravimetric procedures[1,2] a coulometric determination has not been previously reported. The known polarography of tin indicates that coulometric analysis should be feasible in halide media. Reduction of tin(IV) takes place stepwise, to the metal, on a mercury cathode, and coulometric analysis at both reduction stages was undertaken.

EXPERIMENTAL TECHNIQUE

Apparatus

The electrolysis cell (100-ml capacity and with mercury cathode of 16.7 cm^2 area) was the same as that described by LINGANE[3]. Tall-form electrolysis beakers were employed when gold cathodes were used. A constant speed mechanical stirrer was used, with stirring blades adjusted to keep the mercury-solution interface in rapid but smooth motion. Oxygen was excluded by passing a stream of nitrogen through the solution, prior to, and during electrolysis.

The anode was a platinum electrode (1 cm^2) isolated from the test solution by enclosure in a glass tube with a sintered glass bottom. The anolyte (2 *M* sulfuric acid) was maintained at a higher level than the solution in the cathode chamber.

A potentiostat[3] was used to maintain automatically the potential of the cathode at a constant value in reference to a saturated calomel electrode. The quantity of electricity consumed was measured with a hydrogen–nitrogen gas coulometer[4]. A more convenient coulometer which may be employed is the d.c. motor integrator[5]. Current measurements were made with a calibrated multi-ammeter in series with the cathode.

Procedure

The supporting electrolyte (3 *M* sodium bromide, 0.3 *N* hydrochloric acid) alone was placed in the cell, dissolved air was removed with purified nitrogen and the solution was subjected to a preliminary electrolysis with the potential of the cathode at —0.80 V *vs.* S.C.E., to remove traces of reducible impurities. This pre-electrolysis was continued until a small, constant, residual current was observed. The potentiostat was then set to maintain the potential of the cathode at the value used in the determination (—0.40 V *vs.* S.C.E. for reduction of tin(IV) to tin(II), —0.70 V *vs.* S.C.E. for reduction of tin(II) to the metal), the sample solution was added, and the electrolysis was allowed to proceed under automatic control until the current decreased to a constant, minimal value. The total quantity of electricity passed, the electrolysis duration, and the final current were noted.

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Correction for the quantity of electricity associated with the background current was applied by assuming the final electrolysis current was constant throughout the electrolysis.

When a tin amalgam electrode was used, a similar procedure was followed, except that the tin solution, entirely in the stannic form, was stirred with the amalgam several minutes before electrolysis to reduce the tin(IV) to tin(II). The results were calculated as in the previous case, taking into account that twice as much tin was electrolyzed as was introduced. Tin amalgam was prepared by shaking an excess of pure granulated tin (20 to 40 mesh) with mercury, under dilute hydrochloric acid, until a saturated amalgam was obtained.

RESULTS AND DISCUSSION

The investigation of the electrogeneration of stannous tin as a coulometric titrant[6] showed that reduction of stannic tin takes place with 100% current efficiency at a gold electrode in solutions containing a high concentration of bromide ion. This generation of tin(II) for coulometric titration was performed with a large and constant stannic tin concentration (0.2 *M*) at a small electrode. Controlled potential reduction of tin(IV) involves much smaller tin concentrations (0.03 *M*) and relatively large electrodes. These conditions have the effect of increasing the residual current relative to the stannic ion reduction current, causing the reduction to proceed at decreased current efficiency, and necessitating large residual current corrections. In Table I are shown some typical results for the reduction of stannic to stannous tin at gold electrodes.

The current decay during controlled potential electrolysis usually follows the expression[3]:

$$i = i_0 \, 10^{-kt} \qquad (1)$$

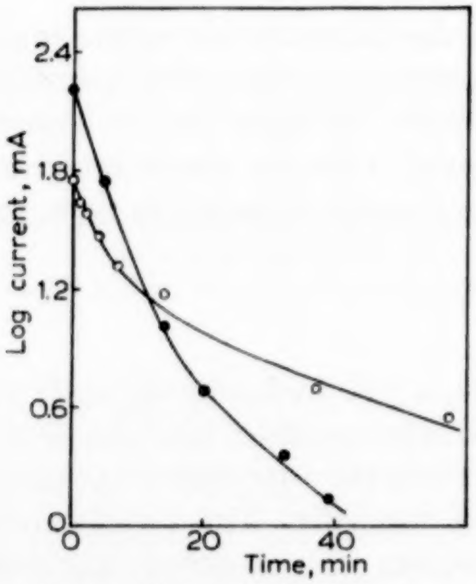

Fig. 1. Typical log current–time curves for the controlled potential electrolysis of tin(IV) at a gold electrode (*ca.* 72 cm²) in 3 *M* sodium bromide and 0.4 *N* hydrochloric acid. About 55.9 mg of stannic tin was reduced at a potential of —0.40 V *vs.* S.C.E.

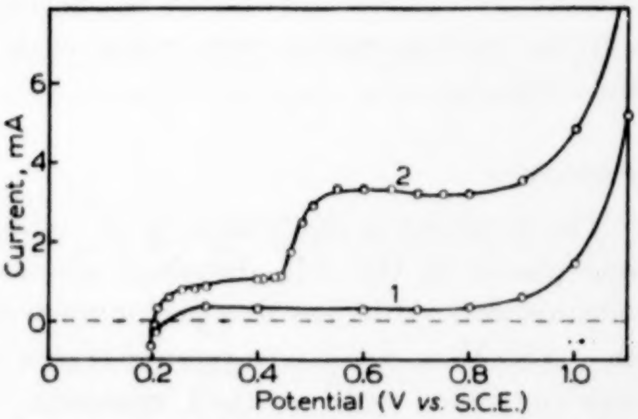

Fig. 2. Current–potential curves for the reduction of tin(IV) on a stirred mercury pool (*ca.* 16.7 cm²). (1) 3.2 *M* sodium bromide and 0.2 *N* hydrochloric acid alone. (2) supporting electrolyte containing 0.002 *M* stannic chloride.

where i is the current at time t, i_0 is the initial current, and k is a constant, whose magnitude depends upon the stirring rate, electrode area, solution volume and temperature. Typical log current *vs.* time curves for the reduction of tin(IV) at a gold cathode are shown in Fig. 1. The initial slope of these curves was used to calculate the k values quoted in Table I. From this k, predicted by the initial slope, (0.061 min^{-1}), the reaction would be predicted to be 99.9% complete in about 50 min. It is evident that the electrolysis does not follow equation (1) however, since the curves deviate significantly from linearity. The decrease of slope of the curves, which occurs after more than 80% of the reduction is complete, is primarily responsible for the long electrolysis durations.

TABLE I

COULOMETRIC DETERMINATION OF TIN ON GOLD ELECTRODES

The solution was 2–3 M in sodium bromide and 0.3–0.6 N in hydrochloric acid. Control potential —0.40 V *vs.* S.C.E. (55.91 mg Sn taken)

Trial	*Volume (ml)*	*Initial current (mA)*	*Final residual current (mA)*	*Electrolysis duration (h)*	*Amount Sn found (mg)*	*k (in min^{-1}) × 10^2*
1[a]	60	11	0.4[c]	13.8	56.18	0.2
2[a]	25	18	0.8[c]	12.1	60.06	0.4
3[b]	100	165	2.2	2	64.33	7.8
4[b]	100	80	0.5	8.3	54.06	6.1
5[b]	100	145	0.3	12	55.84	7.2
6[b]	115	56	1.0	8	54.71	6.3
7[b]	83	22	1.0	9	48.24	4.6
				mean = 56.20 ± 3.71		
				% error = 0.5%		

[a] 14.7 cm^2 flat gold electrode.

[b] 72 cm^2 gold-plated platinum gauze, cylindrical, electrode.

[c] Background current corrections made on the basis of the *pre*-electrolysis residual current (0.064 mA). Correction on the basis of postelectrolysis current would yield very low results.

Deviation of log current *vs.* time curves from linearity has been shown[7] to be caused by kinetic complications of the electrode reactions, such as secondary or competing chemical reactions. The curvature of the curves in this case might be caused by some constant reoxidation of stannous ion at the gold electrode (an example of case IIc, Ref.[7]), which would also give rise to a larger residual current during and following the electrolysis than before it[8]. Correction by assuming a constant background current, equal to the post-electrolysis current, would lead to overcorrection for the background current, and negative errors. Assumption of constant background current equal to pre-electrolysis current causes undercorrection and positive errors.

Another possible kinetic complication might be the presence of two tin complexes in sluggish equilibrium with each other; the reduction at the given electrode potential proceeding through only one of the forms. After most of the easily reducible form has reacted, the rate of the electrode reaction will be governed by the slow, equilibration, step. This would lead to a decrease in the slope of the log current–time curves and anomalously long and varying electrolysis durations.

Therefore, although a coulometric determination of tin based upon the reduction of stannic to stannous tin at a gold electrode is possible, the results obtained are neither very precise, nor very accurate. A large degree of uncertainty is introduced by the background current corrections, which often amounted to 20% of the total coulombs consumed, because of the long electrolysis durations.

Electrolysis of tin(IV) on a mercury cathode offers the advantages of lower residual currents, shorter electrolysis durations by the use of smaller solution volumes and efficient stirring, and the possibility of carrying out a second reduction step, that of stannous ion to tin (amalgam). A current–potential curve for the reduction of tin(IV) at a large mercury pool electrode is shown in Fig. 2. This curve is quite similar to polarograms of tin(IV) taken with a d.m.e.[9]. Since mercury reduces stannic tin in a bromide medium, the first wave corresponds to the reduction of a mercury species (*e.g.* $HgBr_4^{-2}$) rather than tin(IV).

Electrolysis of tin(IV) solutions on a mercury cathode were performed by electrolysis at both —0.40 and —0.70 V *vs.* S.C.E., and typical results of this two-step reduction are shown in Table II. Although the first reduction step is 2.4% incomplete, the second reduction, to tin amalgam, is complete and accurate. The stannic tin is reduced directly by the mercury and the first electrolysis at least partially involves reduction of a mercury species. Apparently some mercury species (*e.g.* Hg_2Br_2) is present which remains unreduced, even at a potential of —0.70 V *vs.* S.C.E. The second reduction step, stannous ion to tin amalgam, is rapid and quantitative, and therefore has greater analytical applicability.

TABLE II

COULOMETRIC DETERMINATION OF TIN ON MERCURY CATHODE

The solution was 3 *M* in sodium bromide and 0.3 *N* in hydrochloric acid, with a volume of 30 ml (46.02 mg tin taken)

Control potential (V vs. S.C.E.)	*Initial current (mA)*	*Residual current (mA)*	*Electrolysis duration (h)*	*Amount Sn found (mg)*
—0.40	50	0.25	3.5	45.15
—0.70	205	0.35	2.1	46.09
—0.40	88	0.25	2.5	45.31
—0.70	240	0.35	2.0	46.33
—0.40	74	0.35	2.5	44.29
—0.70	190	0.55	2.5	45.85

mean = step 1: 44.92 ± 0.42
% error = —2.4%
step 2: 46.09 ± 0.24
% error = +0.15%

To eliminate the time-consuming primary reduction step, a tin–amalgam cathode was employed. An investigation in this laboratory has shown[10] that tin–amalgam completely reduces tin(IV) to tin(II), producing an equivalent quantity of tin(II), in a bromide medium. Of course in the presence of other substances which are reduced by tin–amalgam a mercury cathode must be used. Typical results in Table III demonstrate that 20 to 50 mg of tin in a volume of 30 ml can be determined with an average

TABLE III

COULOMETRIC DETERMINATION OF TIN ON TIN–AMALGAM CATHODE

Electrode potential = —0.70 V *vs.* S.C.E.
The solution was 3.3 *M* sodium bromide and 0.2 *N* hydrochloric acid, with a volume of 30 ml

Initial current (mA)	*Residual current (mA)*	*Electrolysis duration (hours)*	*Amount Sn taken (mg)*	*Amount Sn found (mg)*
300	0.08	3.5	23.01	23.31
190	0.15	2.3	23.01	23.16
210	0.15	2.2	23.01	22.71
			mean = 23.06 ± 0.23, error = 0.21%	
465	0.30	1.0	53.57	54.49
465	0.35	1.0	53.57	53.67
430	0.70	2.0	53.57	52.98
			mean = 53.71 ± 0.52, error = 0.26%	

error of somewhat less than 0.3%, with an electrolysis duration of about 2 hours, with this method. The results show an average deviation of about 1%, mainly because of the uncertainty in the background current corrections.

CONCLUSION

Since tin(IV) is reduced to stannous tin at potentials of —0.3 to —0.4 V *vs.* S.C.E., it will interfere during the controlled potential determination of copper and antimony, unless it is complexed (*e.g.* with tartrate[1]). The reduction of tin(II) at potentials of —0.50 to —0.70 V *vs.* S.C.E. proceeds with 100% current efficiency at a mercury cathode, and may be determined coulometrically in the absence of metals not reduced at these potentials. Pre-reduction at —0.40 V will eliminate interference of copper, antimony and bismuth in this determination. Lead, which is reduced at about —0.50 V, will interfere. Finally, by electrolysis at —0.60 to —0.70 V *vs.* S.C.E., tin may be removed prior to the determination of such metals as nickel and zinc.

ACKNOWLEDGEMENT

The author is grateful to Dr. JAMES J. LINGANE for helpful discussions and suggestions during the course of this work. Appreciation is expressed to the National Science Foundation for a fellowship held by the author.

SUMMARY

The controlled potential coulometric determination of tin in a bromide medium is described. Although the reduction of tin(IV) to tin(II) suffers from complications, and is analytically unsuitable, reduction of stannous tin at a mercury, or tin–amalgam electrode forms the basis of a successful analytical method.

RÉSUMÉ

Une méthode coulométrique, à potentiel contrôlé, est décrite pour le dosage de l'étain, en milieu bromhydrique. La réduction de l'étain(II) à une électrode de mercure ou d'étain amalgamé est tout à fait satisfaisante.

ZUSAMMENFASSUNG

Beschreibung einer coulometrischen Methode mit kontrolliertem Potential zur Bestimmung von Zinn in bromwasserstoffsaurer Lösung. Als Grundlage der Methode dient die Reduktion von Zinn(II) an einer Quecksilber- oder Zinnamalgam Elektrode.

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CARBON PASTE ELECTRODES

APPLICATION TO ANODIC VOLTAMMETRY

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The use of carbon pastes (carbon or graphite intimately mixed with an organic liquid) as substitutes for noble metal electrodes offers several distinct advantages in solid electrode voltammetry. Preliminary reports have dealt with the properties of such electrodes[1,2]. The present study is a critical evaluation of the potentialities of this new electrode system with particular emphasis on its application to routine analysis using standard techniques of anodic voltammetry. Throughout this study an attempt was made to keep the experimental procedures simple while still retaining the best possible analytical results.

Experimental conditions

Polarograms were run by conventional voltage scan techniques using a Leeds and Northrup Model E Electrochemograph. All results were obtained with a stationary electrode configuration in a quiet solution. Typical peak-type polarograms were obtained for which the measurement of peak current (i_p) and half peak potential ($E_{p/2}$) were conventional in all respects.

Half-peak potentials have no special significance but they are preferred for characterization of a given electrode process especially in those cases where the electrode reaction is markedly irreversible. In such cases the peak polarogram is considerably rounded and a precise evaluation of the peak or maximum potential is difficult. However, the measurement of the peak current is rarely impaired and thus the half-peak potential can be located with considerable precision. An open 50-ml beaker was used as the polarographic cell.

Buffer solutions and background electrolytes were prepared from c.p. chemicals in all cases. The Britton and Robinson buffer solutions were prepared according to the directions given by MULLER[3]. For some of the work, the ionic strength was "swamped" by the addition of 0.2 M Na_2SO_4.

The organic electroactive compounds were either Eastman white label or purified samples kindly supplied through the courtesy of Mr. JOHN TINKER, E. I. du Pont de Nemours and Company. Since many of the amines are susceptible to air oxidation their stock solutions were made from air free water. The solutions were not deaerated prior to or during the run.

Preparation of carbon pastes

Carbon rods have been investigated for some time. To eliminate large residual currents observed with these electrodes it is necessary to impregnate them with wax[4,5]. It was reasoned that a thick paste of carbon with a water immiscible, non-electroactive liquid might function as well as a wax-impregnated rod.

An ideal pasting liquid would be one which was completely water immiscible, of very low volatility and which contained no electroactive impurities. Among the liquids investigated (from which successful electrodes can be prepared in all cases) were carbon tetrachloride, bromoform, benzene, mixed trimethylbenzenes, ethylnaphthalene, bromonaphthalene and Nujol. The last two named liquids seem to present the best compromise of the desired characteristics. Electrodes prepared from these pastes are described in detail. It should be pointed out that probably any non-electroactive liquid will function as the pasting material. A liquid of low volatility is to be preferred in order that the electrode may be used for long periods without evaporation changing the surface character. If the electrode is to be used for aqueous solutions, the liquid must be highly immiscible with water.

Several varieties of carbon and graphite were evaluated. Nuchar, Norite and vegetable charcoal were found to be too gritty to give smooth pastes. Acheson Grade 38 powdered graphite and spectroscopic graphite (United Carbon Products were ideally suited. Acetylene black, 50% compressed ("Shawinigan Black") commonly employed as a battery mix was also found to be very satisfactory. All of the data reported here were with Acheson Grade 38 graphite.

Pastes were prepared in the simplest possible manner by hand mixing measured quantities of carbon and organic liquid. A typical mixture contained 6 g of powdered graphite and 4 ml of bromonaphthalene. This paste was moderately thick and ideally suited for pool electrodes.

The construction details of the electrode proper are shown in Fig. 1. The Teflon plug was machined to a well configuration about 1/4" deep and 1/4" in diameter. The dimensions are in no way critical and can be altered to suit sensitivity requirements. A fine bore hole through the back of the Teflon plug admits a platinum wire electrical contact. Other materials could probably be used in place of Teflon but it is particularly useful in that it is wetted by few materials and easy to clean. A standard taper glass joint surrounds the electrical connection and insulates it from contact with the solution. The paste was tamped into the well until flush with the edges. Excess paste was removed by smoothing with a spatula. Any paste remaining on the rim can be easily wiped off with Kleenex or similar material. A remarkably smooth carbon paste surface is obtained with this simple procedure. Bromonaphthalene pastes form exceptionally smooth surfaces and are very easy to handle. Nujol pastes are somewhat sticky and a bit more difficult to work with. They have, however, some distinct advantages as discussed later.

The electrode was used in an inverted pool configuration, *i.e.*, with the Teflon plug dipping down *ca.* 1–2 cm below the level of the solution. Fig. 2 shows an overall picture of the electrode.

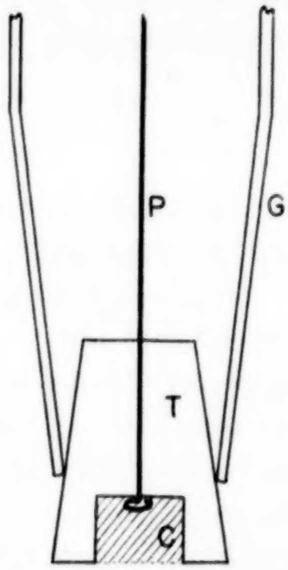

Fig. 1. Carbon paste electrode holder. T. Teflon plug with well 1/4 inch diameter, 3/16 inch deep. C. Carbon paste, P. Platinum wire, G. Glass tube.

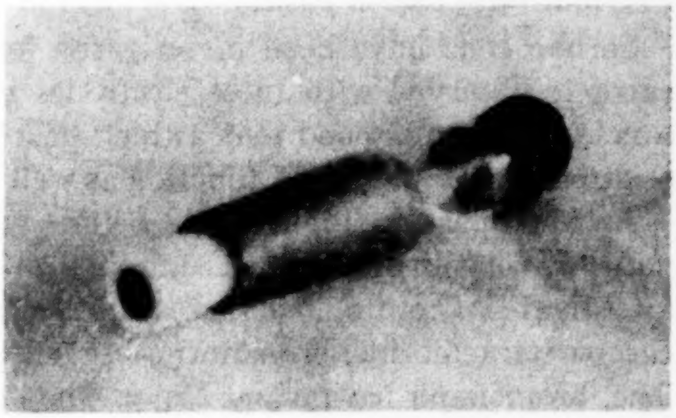

Fig. 2. Carbon paste electrode.

Using the terminology carbon paste electrode, the natural abbreviation would be CPE. However, this may be somewhat confusing in that the rotating platinum electrode has long been abbreviated RPE. To avoid this difficulty, it was decided to adopt the term CE (carbon electrode) followed by the type of pasting liquid. Thus, the bromonaphthalene paste electrode will be abbreviated here and any subsequent publications as CE–BnP (Carbon Electrode – Bromonaphthalene Paste). Similarly, the Nujol paste electrode is designated CE–NjP.

RESULTS AND DISCUSSION

(a) Anodic range of the CE–BnP

TABLE I

ANODIC RANGE OF THE CARBON PASTE ELECTRODE IN VARIOUS BACKGROUND MEDIA

Media	*Potential when $i_r = 2\ \mu A$ (V vs. SCE)*
1 *M* KCl	1.10
0.1 *M* KCl–HCl, pH 2.5	1.08
1 *N* HCl	1.02
0.1 *M* NaAc–HAc	1.27
1 *M* Na_2SO_4	1.28
0.2 *N* H_2SO_4	1.30
B.R.B.[a] + 0.2 *M* Na_2SO_4, pH 2.4	1.30
B.R.B. + 0.2 *M* Na_2SO_4, pH 4.8	1.30
0.2 *N* NaOH	0.87

[a] Britton and Robinson buffer.

Table I shows the useful anodic range of the CE–BnP in a variety of supporting electrolytes. The useful range was arbitrarily set at that potential *vs.* SCE at which the residual current exceeded 2 μA. One of the most desirable characteristics of carbon paste electrodes is the extreme low level and flatness of the residual current over the entire useful potential range. For instance in the Britton and Robinson buffer solution (pH *ca.* 2.5, 0.2 *M* in sodium sulfate), the residual current at +0.10 V *vs.* SCE is about 0.02 μA and has only increased to 0.1 μA at +1.0 V *vs.* SCE with the CE–NjP. This same residual current behavior is found in almost all supporting electrolytes and with all types of pastes. Since the important parameter for analytical usage of solid electrodes is the ratio of faradaic current to residual current, carbon paste electrodes show considerable promise in this respect. The residual currents encountered are much lower than those at noble metal electrodes where oxide formation and history effects are prevalent.

The anodic limits of most of the pastes examined are similar and in general equal or superior to those of platinum. The CE–NjP has a slightly greater anodic range than that of the CE–BnP listed in Table I for Britton and Robinson buffer. Due to the excellent residual current level, the entire anodic range is available for study.

(b) Pretreatment of electrodes

Starting with a fresh paste electrode, no pretreatment whatsoever is needed. In general, after a polarographic run, the electrode is simply washed with a stream of distilled water. In some cases, for instance where reproducibility data is desired on the same solution, it is only necessary to stir the solution to sweep away oxidation products before beginning the next run. On the other hand, the oxidation of some compounds like naphthols and aromatic thiols seems to form films on the electrode surface (this is common behavior for the electro-oxidation of these materials at solid electrodes). In these cases it may be wiser to build a fresh electrode for each run, although cathodic treatment at *ca.* —0.4 V prior to the next run seemed helpful in obtaining reproducibility in some cases.

(c) Temperature effects

Since carbon pastes represent a new form of solid electrode it seemed desirable to check the temperature coefficient of limiting currents. Fig. 3 shows the linear varia-

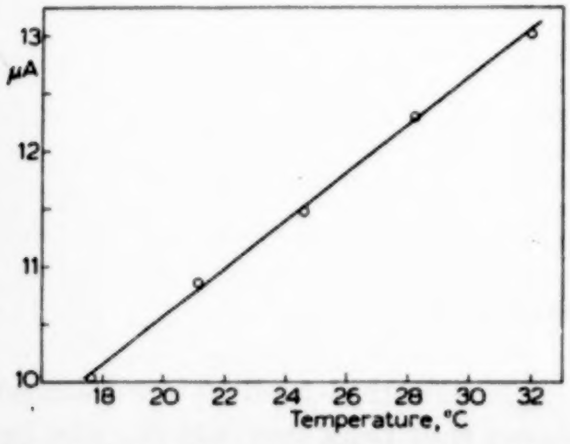

Fig. 3. Variation of peak current with temperature for 10^{-3} *M* $K_4Fe(CN)_6$ in 1 *M* KCl.

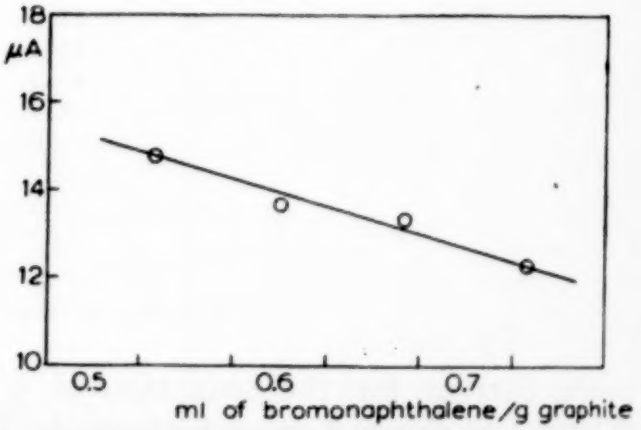

Fig. 4. Variation of peak current with paste composition for 10^{-3} *M* $K_4Fe(CN)_6$ in 1 *M* KCl.

tion of peak current with temperature over the temperature range of 18–32°. In the terminology of previously reported data, this represents a temperature coefficient of about 2% per degree.

(d) Effects of variation in paste composition

The peak current is proportional to the surface area of the electrode. As the ratio of organic liquid to carbon increases, the peak current decreases. This is seen in Fig. 4 for bromonaphthalene paste. These currents are for the oxidation of 10^{-3} *M* ferrocyanide in a background of 1 *M* KCl. Each point represents an average current for three individual pastes with the indicated composition. Clearly the more "dry" paste is advantageous in terms of sensitivity. In addition, such pastes are somewhat easier to handle.

Attempts were made to dilute the carbon content of the paste without changing the fluidity characteristics by substituting filler material for the carbon. All of the materials tried, celite, barium sulfate, alumina, and starch were unsatisfactory since they separated from the paste proper immediately upon immersion in the liquid. Thus, it was not possible to evaluate the dependence of peak current on the available carbon content. On the other hand, the electrochemical area obtained from linear diffusion studies on ferrocyanide oxidation was found to be approximately the same as the measured geometrical area.

(e) Reproducibility and storage of electrodes

Since carbon paste electrodes can be prepared with such ease (a fresh electrode can be made in 2–5 min), it is possible to use new electrodes for each run or to arrange a suitable storage technique for one electrode. The reproducibility of each of these techniques was examined.

Normally a paste is prepared in a large batch. Freshly packed electrodes were prepared on 9 consecutive days from the same batch of bromonaphthalene paste and the peak current for the oxidation of $5 \cdot 10^{-4}$ *M* N,N-dimethyl-*p*-phenylenediamine (DPP) was checked on each electrode. Table II shows that peak currents (i_p) can be reproduced to about 6%. It is rather surprising that the surface areas are thus reproducible.

TABLE II

REPRODUCIBILITY OF THE CARBON PASTE ELECTRODE AREA ON FRESHLY PREPARED ELECTRODES

Peak height (μA)	*$E_{p/2}$ vs. SCE (V)*
14.4	0.455
16.6	0.426
17.2	0.427
15.4	0.433
16.2	0.430
15.0	0.437
14.4	0.441
16.2	0.439
14.8	0.444

Average 15.6, average deviation 5.7%.

TABLE III

PEAK CURRENT (µA)

Day	*CE–BnP*	*CE–NjP*
1	12.27	16.34
2	12.24	16.82
3	12.20	17.00
4	11.92	16.68
6	12.20	17.02
7	11.80	16.66
8	11.50	16.16
9	11.70	
14	12.30	
15	11.87	
17	12.05	
18	11.90	
21	11.55	
22	11.80	
Average	11.95	16.67
Average deviation	0.22	0.24
% Average deviation	1.84	1.44

Two storage techniques were investigated: *(a)* the electrode was kept in a sealed atmosphere of bromonaphthalene vapor, and *(b)* kept under distilled water when not in use. Storage in an open beaker under distilled water turned out to be much more reproducible and convenient. Table III shows the reproducibility of i_p for a CE–BnP stored for 22 days and a CE–NjP for 8 days. Two different electrode reactions were used; oxidation of $1 \cdot 10^{-3}$ *M* ferrocyanide in 1 *M* KCl for the CE–BnP, and oxidation of $5 \cdot 10^{-4}$ *M* *o*-dianisidine in pH 2.5 buffer for the CE–NjP. It is readily seen that long range reproducibility is a little less than ± 2%. The short time reproducibility of carbon paste electrodes is much better than this value. Using a standard comparison polarogram run concurrent with an "unknown", reproducibility of about ± 0.5% is attainable. For instance, Fig. 5 shows three successive polarograms for the oxidation of *o*-dianisidine in buffered medium. This is an actual chart recording and it can be seen that the three polarograms are almost superimposable over the entire voltage span. In general successive polarograms seem to have a short time reproducibility of about ± 0.2%.

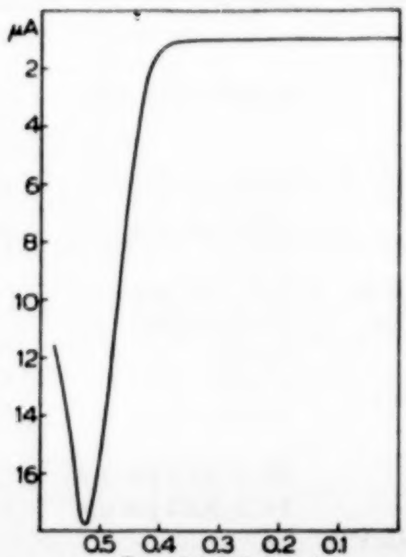

Fig. 5. Successive reproducibility of CE–BnP for oxidations of *o*-dianisidine.

TABLE IV

Constancy of i_p/C *versus* concentration for DPP in 0.1 *M* KCl–HCl at pH of about 2.5

Concentration *(M · 10⁵)*	*Peak current* *(µA)*	i_p/C *(µA)*
1.0	0.316	3.16
2.0	0.663	3.31
4.0	1.30	3.25
6.0	1.96	3.27
8.0	2.58	3.23
10.0	3.25	3.25
14.0	4.48	3.20
20.0	6.30	3.25
		Dev. 1.2%

Constancy of i_p/C *versus* concentration for oxidation of $FeSO_4$ in 1 *N* HCl

Concentration *(M · 10⁴)*	*Peak current* *(µA)*	i_p/C *(µA)*
1.0	1.35	1.35
2.0	2.75	1.38
3.0	3.99	1.33
4.0	5.35	1.36
5.0	6.50	1.30
6.0	7.53	1.26
10.0	12.8	1.28
		Dev. 2.8%

TABLE V

SURVEY OF OXIDATIONS AT CARBON PASTE ELECTRODES

Electroactive species	*Background*	*Type electrode*	$E_{p/2}$ *(V vs. SCE)*	
A. Inorganic				
1. $Fe(CN)_6^{-4}$	BRB[a]	CE–BnP	(+)0.21	
2. Fe^{+2}	1 *N* HCl	CE–BnP	0.75	
3. I^-	BRB[a]	CE–NjP	0.49	
4. I^-	1 *N* H_2SO_4	CE–NjP	0.44	
5. Tl^+	1 *N* NaOH	CE–NjP	0.32	
6. NO_2^-	BRB[a]	CE–NjP	0.89	
B. Organic				
1. 1-Naphthylamine	BRB pH 5.1	CE–BnP	(+)0.53	
2. 1-Naphthol	BRB[a]	CE–BnP	0.63	
3. 1-Amino-7-naphthol	BRB[a]	CE–BnP	0.45	
4. 5-Amino-2-naphthalene sulfonic acid (1-6 Cleves acid)	BRB[a]	CE–BnP	0.52	
5. 7-Anilino-1-naphthol 3-sulfonic acid (phenyl gamma acid)	BRB[a]	CE–BnP	0.50	
6. Aminoazobenzene	BRB pH 4.1	CE–BnP	0.74	
7. 3,4-Diamino toluene	BRB pH 4.4	CE–BnP	0.28	
8. 2,4-Diamino toluene	BRB[a]	CE–BnP	0.71	
9. *p*-hydroxydiphenylamine	BRB pH 4.4	CE–BnP	0.22	
10. *p*-ethoxydiphenylamine	BRB pH 2.6	CE–BnP	0.63	
11. *o*-Dianisidine	BRB[a]	CE–BnP	0.46	
	BRB[a]	CE–NjP	0.46	
12. Dimethylaniline	BRB[a]	CE–BnP	0.68	(1st wave)
			0.92	(2nd wave)
13. *o*-Tolidine	HCl–KCl pH 2.5	CE–BnP	0.51	
14. N,N-dimethyl-*p*-phenylenediamine (DPP)	HCl–KCl pH 2.5	CE–BnP	0.45	

[a] Britton-Robinson buffer solution A containing 0.2 *N* Na_2SO_4, pH 2.4.

Table IV shows the constancy of i_p/C *vs.* concentration for the oxidation of typical organic and inorganic species at the CE–BnP. These results are quite good and compare very favorably with previous stationary solid electrode data. Nujol pastes (and, for that matter, pastes of all other liquids examined) show essentially the same results.

Table V summarizes the spectrum of anodic oxidations examined at carbon paste electrodes. In general, half-peak potentials at carbon paste electrodes are comparable but not always identical with those obtained at platinum electrodes. The half-peak potentials of many of the organic compounds listed in Table V agree within ± 5 – 10 mV of the corresponding values at platinum. In the case of inorganic oxidations, somewhat greater differences exist in some cases. It has also been found that the half-peak potentials of inorganic compounds vary in some cases with the particular carbon used. This problem is of great interest and will be discussed in detail later. From the practical analysis viewpoint, using Acheson Grade 38 graphite a series of highly reproducible and self-consistent $E_{p/2}$'s can be obtained.

ACKNOWLEDGEMENT

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SUMMARY

The use of carbon paste electrodes (carbon of graphite intimately mixed with an organic liquid) as substitutes for noble metal electrodes is described. This method offers several distinct advantages in solid electrode voltammetry and can be applied to routine analysis using standard techniques of anodic voltammetry.

RÉSUMÉ

Les auteurs proposent l'emploi d'électrodes de carbone (charbon ou graphite intimement mélangé à un liquide organique) pouvant être substituées aux électrodes de métaux nobles; elles présentent plusieurs avantages et elles peuvent être appliquées à la voltammétrie anodique.

ZUSAMMENFASSUNG

Elektroden aus Edelmetallen können vorteilhaft durch solche aus einer Graphitpaste ersetzt werden. Ihre Anwendungsmöglichkeit bei der anodischen Voltammetrie wird beschrieben.

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Short Communications

A preheating, automatic, self-flushing still

In titrimetric investigations at high precision[1,2] a primary requirement was a source of grease-free distilled water of very low halogen and sulphur content. The primary objectives in the original design were therefore a still and dispenser completely free from lubricated joints or taps, without rubber connections or bungs, and a means of eliminating vapour and spray entrainment. The quality of output proved to be surprisingly high, particularly in respect to nitrogen content, and after incorporation of filtration and dust protection the product also proved to be and to remain sterile. This led to the development of the still, referred to in a recent communication[1], which combines the following advantages.

(1) The economy of a preheated feed, which reaches the heater at boiling point. *(2)* The convenience of safe automatic working. *(3)* The high quality of product produced by all glass/quartz construction, a high reflux ratio, the virtual elimination of entrainment, and the long vapour path. *(4)* The economy of space and the facility of mounting (one clamp at either end) by placing the still high up on a wall out of the way. *(5)* Automatic cleaning, any sludge or deposit formed being carried away through the overflow. *(6)* Security of operation. If water supply pressure drops, although the distillate temperature will rise, the still continues to operate in safety so long as any water continues to flow. Should the supply cease entirely, the top fusible link will

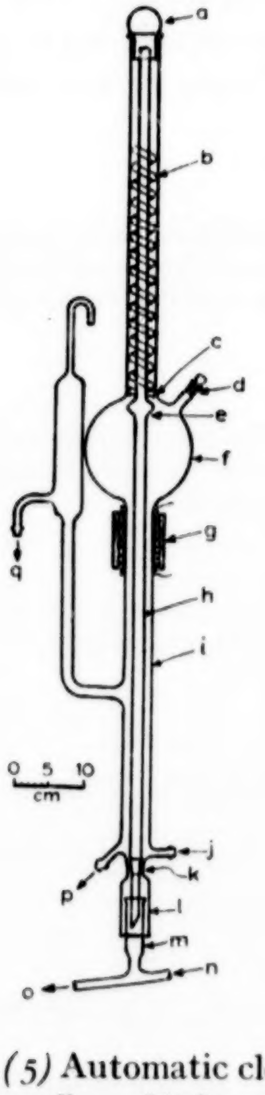

Fig. 1. Diagram of the preheating, automatic, self-flushing still. a. Deflector dome. b. Spiral of 7 mm borosilicate. c. 3-point spacer fused to inner tube. d. Inlet for chemical cleaning B-14 joint. e. Spray baffle. f. Boiling chamber (1-litre bulb). g. 800–1000 Watt nichrome ribbon heater. h. 15-mm thin wall borosilicate or quartz. i. 40-mm thick wall borosilicate. j. Cold feed. k. B 14 borosilicate socket, quartz or borosilicate cone sealed with Apiezon wax. l. Sheath. m. Collector. n. From other stills. o. To quartz filter and storage. p. Flushing (normally closed). q. Overflow.

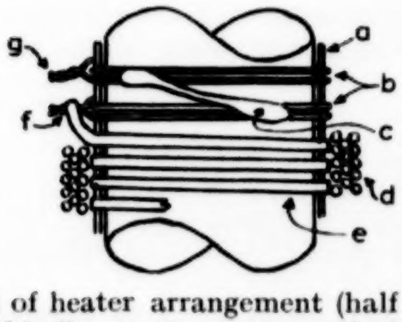

Fig. 2. Detail of heater arrangement (half size). a. Mica. b. 14 s.w.g. copper binding posts. c. 2.5-cm fusible link of 14 s.w.g. 60/40 cored solder. d. Asbestos lagging. e. 800–1000 Watt nichrome ribbon element. f. Silver solder. g. Mains connection.

blow just before the water level falls to heater level, thus preventing damage to heater element or glass.

Construction

The construction is illustrated in Figs. 1 and 2. The heater is wound from nichrome ribbon in a single layer on mica. Each end is silver soldered to a binding post made from two turns of 14 s.w.g. copper wire with the ends twisted together not too tightly. This in turn is connected through a 2.5-cm fusible link made of 14 s.w.g. 60/40 lead/tin resin-cored solder wire to a second binding post. The mains leads are connected to the outer pair of binding posts. If asbestos tape or string is used to cover the winding, it should be heated to remove dressing and moisture before the element is operated, else the upper link tends to blow in the evolved steam. The upper link should not be covered with asbestos. The overflow height should be so adjusted that the water level when cold lies between the top of the heater and the bottom of the boiling chamber, and the length of the overflow chamber should be adequate to permit flushing of the whole boiling chamber when the overflow is closed. The deflector dome at the top should be a fairly loose fit and be lightly seated by grinding. This constitutes a safety valve in case of sudden excessive bumping. When the still surfaces are very clean, "bumping", or explosive boiling, is liable to occur. It is important to cut off all delivery tubes at an acute angle to avoid liquid locks. The unit is vented to atmosphere only at the bottom of the inner tube where the distillate drips into the collector which is sheathed to prevent access of dust or heavy fumes. The inner tube is interchangeable: borosilicate gives excellent quality water and, if thin wall tubing is used, good heat transfer; quartz gives an even better, boron-free distillate, but heat transfer is less efficient. For ease of removal, the joint is lightly sealed with Apiezon wax which can be released by warming, but, being at the coldest part of the unit, does not contaminate the feed. The collector manifold (a battery of stills is actually in use) carries the distillate to an encapsulated porosity 3 sintered quartz filter, thence to a 20-litre borosilicate storage bottle. Supplies are dispensed from a fully protected all-glass syphon arrangement. It is convenient to arrange the plumbing so that overflow and flushing outlets join through a Y-piece, the flushing outlet normally being closed with a screw clip. A screw clip on the combined outlet permits flushing of the boiling chamber.

Cleaning

Sludge, humus, loose and siliceous and ferruginous deposits are normally carried away in the overflow, but hard scale builds up gradually. This is removed by disconnecting the collector manifold, charging the still with 800 ml of hot 5 – 10% potassium acid sulphate through the side arm on the boiling chamber, and boiling for 10 min. This is followed by thorough flushing with water and steaming out with feed and overflow closed and the boiling chamber half filled. If the deposit is highly siliceous, preliminary boiling with 800 ml of hot 5% caustic soda loosens the deposit ready for the acid treatment.

Performance

One still in operation for six years has produced some 5000 l without breakdown other than once blowing off the deflector dome and twice blowing a fusible link. The cost of running is approximately 1.2 pence (1.4 cents) per l, and the distillation rate is 800–1000 ml per hour per still. The quality may be judged from the figures below. The distillate naturally contains carbon dioxide, and so is not suitable for conductivity work. However, by allowing partial steam off at the top by inserting a very fine nylon hair in the dome seating, and cutting down the cold feed so that the distillate is delivered at above 65° into carbon dioxide free containers, very little carbon dioxide is dissolved in the distillate, and the dissolved solids from the glass show only a slight increase.

TABLE I

Analysis of feed p.p.m.		*Analysis of distillate p.p.m.*	
Chloride	13	Chloride	< 0.001
Nitrate	1.2	Sulphate	< 0.001
Temporary hardness	26–52	Total nitrogen	< 0.0001
Permanent hardness	30–34	Total solids	
Saline ammonia	0.024	(borosilicate inner tube)	0.002
Albuminoid ammonia	0.024–0.048	(quartz inner tube)	0.0001
Total solids	100–130		
Suspended solids	2–5		

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1 E. Bishop, *Anal. Chim. Acta,* 20 (1959) 315.
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Low pressure method for carbon analysis in steels: a note

The low pressure method for the analysis of less than 0.1% of carbon in steels is well-established[1]. As described recently by Cook and Speight[2], it is both simple and reliable.

However, when an apparatus similar to that of Cook and Speight was set up in our laboratories, some difficulty in its operation was observed: when the multiple coil trap for freezing out carbon dioxide was immersed in liquid air—which is the coolant used here—oxygen from the gas stream condensed in it. The temperature of the liquid air was about —188.5°, at which temperature oxygen has a saturated vapour pressure of about 405 mm[3]. Owing to this lowering of pressure and the condensation of oxygen, it was difficult to maintain a steady outflow of the gas from the trap and prevent a back suction of atmospheric air. Moreover, the liquefied oxygen

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in the multiple coil trap tended to rise with the gas stream, especially during evacuation, resulting in quick evaporation at the exposed parts followed by a localised increase of pressure; this involved the risk of damage to the apparatus.

It was, therefore, necessary to design a trap which when used with liquid air as the coolant would be free from these difficulties.

After some trials the trap shown in Fig. 1, which is similar to that described by WELLS[4], was constructed for use with liquid air as the coolant. The inlet end of the trap was fused to a vacuum tested stopcock S_1 and the exit end to a similar three-way stopcock (S_2). One lead of S_2 served as the gas outlet through the moisture absorbers, while the other was connected by means of an interchangeable ground glass joint to the calibrated carbon dioxide pressure measuring unit. The rest of the apparatus followed the established pattern[2].

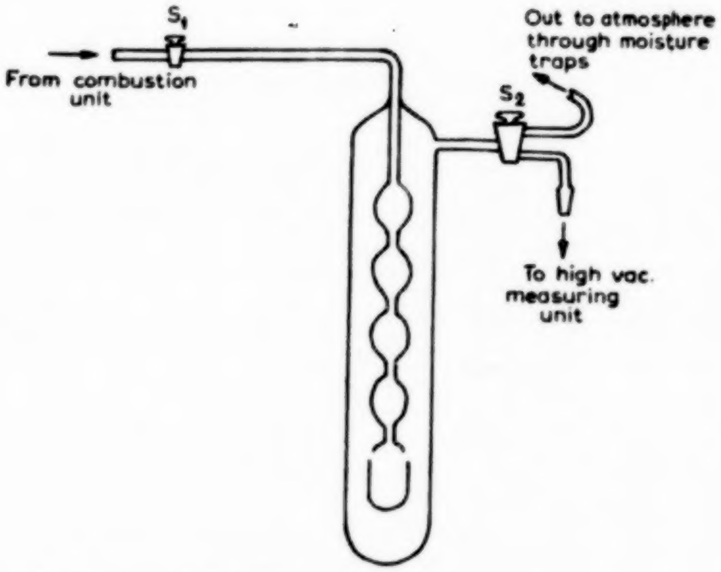
S_1
From combustion unit
Out to atmosphere through moisture traps
S_2
To high vac. measuring unit

Fig. 1. Modified trap for CO_2 condensation.

Since oxygen started condensing in the trap when the latter was immersed in liquid air, the procedure had to be modified as follows.

After the initial flushing out of the combustion system with purified oxygen, stopcocks S_1 and S_2 were closed and the trap was immersed in liquid air. Oxygen gas continued to bubble out of the safety mercury bubbler included in the gas line, keeping the system up to stopcock S_1 under a positive pressure of about 5 cm of mercury. When the trap had attained the temperature of liquid air, the oxygen flow rate was increased to the desired value and the sample introduced for combustion. Stopcock S_1 was then manipulated so as to maintain a constant flow of gas past the sample boat into the trap. During this period, the system remained under a slight negative pressure of 1–1.5 cm of mercury, the mercury bubbler indicating the internal pressure. A second liquid air flask was raised under the calibrated measuring coil, stopcock S_1 was closed after the usual combustion period, and S_2 was opened gently to connect the trap with the evacuating pumps through the measuring unit. Pumping out condensed oxygen from the trap and returning the measuring unit to its original evacuated state required 4–5 minutes. Frozen carbon dioxide was then transferred from the trap to the coil in the usual way and its pressure was measured.

The time of analysis was slightly longer, but the use of liquid air instead of liquid oxygen as the coolant caused no difficulty.

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